DETERMINATION OF THE RELATIONS BETWEEN STRUCTURE

AND

RADIATION STABILITY OF ARYL ETHER FLUIDS

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FOREWORD

ABSTRACT

Aryl ethers are quite resistant to radiolytic degradation. The principal physical property change observed as the result of radiolysis is a rather rapid increase in viscosity. Chemically, weakly acidic and relatively low-boiling compounds are formed.

Aryl ethers such as bis[m - (m -phenoxyphenoxy)phenyl] ether, m -bis(m-phenoxyphenoxy)benzene and Monsanto DS 124 are more stable toward radiolytic degradation than diphenyl ether or diphenoxybenzenes if the formation of benzene and phenol is used as a criterion for radiation stability. If, however, the change in viscosity is a measure of stability, then all of these ethers possess the same magnitude of stability.

The radiolytic degradation mechanisms of diphenyl ether were studied extensively. These mechanisms involve polymerization reactions and scission reactions of the carbon-oxygen bond of the ether with the formation of phenyl and phenoxy-free radicals. The reaction of these free radicals with diphenyl ether explain most of the chemical changes observed. The reaction of the phenyl radical at the ortho position of the diphenyl ether results in the formation of phenol; however, a small amount of this radical forms benzene. The remainder of the phenyl radicals appear to react at the meta and para positions of the ether molecule to form biphenylyl phenyl ethers. The mode of the phenoxy radical reactions is less clear; however, they appear to react with diphenyl ether to form isomeric diphenoxybenzenes.

The rate of disappearance of diphenyl ether decreases as the radiation dose is increased and becomes nearly constant ($-G_m = 0.4-0.5$) at high doses. The ether consumed to form polymer increases as the radiation dose is increased and appears to become constant at high doses. The polymeric material is a glassy brown solid with a rather high molecular weight.

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RADIOLYSIS OF DIPHENYL ETHER

I.   INTRODUCTION

In recent years considerable attention has been given to the potential uses of polyphenyl ethers. These compounds have been shown to be relatively stable at high temperatures (up to 1000°F.), to resist oxidation and to possess good lubricating properties. They also are quite stable in radiation environments. The meta-linked polyphenyl ethers possess a rather wide liquid range and this, coupled with the above mentioned properties, makes these compounds potentially usable as lubricants and as hydraulic and heat transfer fluids in high temperature and radiation environments.

Previous work related to the behavior of the polyphenyl ethers in radiation environments has been concerned primarily with ascertaining the changes in properties such as viscosity, oxidation stability, thermal stability and lubricity.[1,2] These studies have shown that the aryl ethers are quite stable toward radiation. The most significant changes induced by radiation are those related to viscosity and oxidation stability. However, the latter is influenced to a greater extent by thermal degradation than by radiolytic degradation.

Viscosity increases induced by radiolysis are undoubtedly the result of polymerization reactions and appear to be the most significant of the observed physical changes. None of the work reported in the literature gives any indication of the mechanisms by which the degradation reactions occur.

If the more predominant mechanisms responsible for the radiolytic degradation of polyaryl ethers could be ascertained, then it might be possible to prepare ether compounds possessing a greater degree of radiolytic stability without sacrificing other desirable properties of the ethers. Since the polyaryl ethers are rather difficult to work with analytically, it was proposed that a detailed study of diphenyl ether degradation mechanisms be made. Information derived from these studies could then be used as an indication of some of the mechanisms probably occurring in the radiolysis of the ether homologs of higher molecular weight.

The chemical literature is very meager in regard to work concerning the effects of radiation on diphenyl ether. Kharasch, Stampa and Nudenberg[3] have reported briefly some work related to the effects of ultraviolet radiation on diphenyl ether. The results of this work are rather inconclusive.

Wagner and Towle[4] have reported the effects of high-energy electron bombardment on diphenyl ether, diphenyl methane, etc. This work was concerned chiefly with the identification of radiolytically formed products. Components identified as the result of this work included hydrogen, benzene, phenol, biphenyl, a phenyl biphenyl ether, and a diphenoxybenzene, in addition to ten unidentified high-boiling materials. Further discussions of this work will be considered in later sections.

In recent years Schmidt-Collérus and co-workers at the Denver Research Institute have conducted studies concerning the effects of gamma radiation on alkylpolyphenyl hydrocarbons.[5,6] In a previous report from the Denver Research Institute, Schmidt-Collérus and Bohner summarize the initial work conducted on the radiolysis of aryl ethers.[7] Parts of the latter are incorporated into this report whenever related to the discussions.

II.   BACKGROUND - PRESENT CONCEPTS REGARDING THE RADIATION CHEMISTRY OF AROMATIC COMPOUNDS

The literature on the radiation chemistry of aromatic compounds contains several comprehensive reviews.[8,9,10,11,] This discussion is intended to provide a general background from which a better understanding of the reported research work can be derived.

The objective of radiation chemistry is to define the processes that cause observable changes when a material is subjected to the influence of radiation. Current concepts have tended to narrow the field of radiation chemistry to the study of processes resulting from high-energy electromagnetic radiations and to exclude many of the concepts of photochemistry. Often the latter exclusion is justified; however, it would be rather difficult to stipulate at what energy of radiation the concepts of photochemistry cease to apply to the present concepts of radiation chemistry.

Electromagnetic radiations below a wave length of about 100 Å are called X-rays or gamma rays depending upon their origin. The energy of these radiations when passing through matter can be dissipated in three primary ways; namely, pair production, Compton scattering and photoelectric absorption. These processes are briefly defined below:

(a) Pair production is the process by which a photon forms an electron and a positive particle (positron). For this process to occur, the incident photon must possess at least 1.02 Mev. of energy. If pair production occurs, the energetic electron and positron lose their energy by causing ionization and excitation. The positron is destroyed by combination with an electron to give two photons with an energy of 0.5 Mev. The latter is designated as annihilation radiation.

(b) Compton scattering occurs when photons lose part of their energy by inelastic collisions with electrons from atoms. The ejected electrons cause ionization and excitation while the scattered photon, though of reduced energy, undergoes further Compton scattering and energy reduction by photoelectric absorption. Compton scattering is of primary importance when gamma rays interact with materials of low atomic number. When these gamma rays possess energy in excess of 1 Mev. almost all of the ejected electrons result from Compton scattering.

(c) Photoelectric absorption is the process whereby the incident photon is absorbed by an atom and a fast electron is ejected. This absorption is greatest for radiation of low energy interacting with material of high atomic number.

The above processes are of primary interest to the physicist. To the chemist, it is the results of these physical processes that are of interest. These processes lead to ionization and excitation. Under the influence of high-energy radiation, there is sufficient energy available to cause the excitation or ionization of any electron in the molecule. In aromatic liquids ionization presumably can occur but cannot be measured accurately. Such ions, if formed, are thought to be neutralized to yield the parent molecule in an excited state.[12] The effects of radiation on aromatic molecules, therefore, appear to result from the action of excited molecules. The excitation affects the entire molecule and if a reaction is to occur it may or may not take place in the track of the incident particle.

The chemical effects produced in liquids during radiolysis are thought to be initiated by two differently excited species.[13] The one, formed in the primary ionization process, usually is in its lowest excited state and can diffuse away from the point of formation either as an excited molecule or as a deactivated molecule. Deactivation occurs through photon emission or dissociation into a free radical, the latter resulting in a chemical reaction. The other, formed through a charge neutralization process, is in a much higher energy state than the one formed by direct excitation and decomposes rapidly into radicals before leaving its point of origin.

The excitation energy can be transferred from one molecule to another. The mode of energy transfer is controversial and any one or all of the transfer mechanisms listed below may contribute in a particular system.[10] This transfer of energy* may occur by:

---

*Energy transfer should not be confused with the term "Linear Energy Transfer" or LET which is used frequently in describing the linear density of events occurring in a radiation track. LET effects need not be considered here since they are dependent upon the type of radiation, but it does affect the amount and type of yield products found in the radiolysis of aromatic compounds.[14]

(a) simple collision,

(b) emission of a photon which is absorbed by another molecule,

(c) inductive resonance, or

(d) excitation transfer.

Excited molecules, whether formed by energy transfer or by primary radiation, can lose energy by fluorescence or internal conversions to give strongly vibrating lower electronic states. The vibrational energy can be lost by collisions. The excited species can decompose to yield molecular products by a unimolecular process or by reaction with other excited species. Decomposition to form free radicals is also possible.

The formation of free radicals and their subsequent reactions provide a means of accounting for many of the products formed during the radiolysis of aromatic liquids. Since free-radical mechanisms can account for many of the products formed in the condensed state, it is logical to assume that the actual rate of radical formation is much greater than that indicated by any of the methods used for the detection of free radicals. The highly-reactive radicals can recombine within the solvent cage (environment of immediate reaction), thus leading to no observable reaction. This is known as the Franck-Rabinowitch effect. The more energetic or less reactive radicals can escape from the cage and thus can enter into observed reactions.

In the rigid structure of the solid state the Franck-Rabinowitch effect is reduced and the identification and quantitative measurement of free-radical formation is possible with electron spin resonance techniques and ultra-violet absorption spectroscopy. The Franck-Rabinowitch effect is more operative in the liquid state, thus making it impossible to measure the total degree of radical formation by these or other methods; however, methods are available whereby the radicals escaping from the solvent cage can be detected and quantitatively measured. These methods utilize either the effects of the radicals formed on the polymerization of certain monomers or the radical-combination reactions of such materials as diphenylpicrylhydrazil (DPPH) or iodine and are known as radical-scavenger techniques.

The chemistry of many free-radical reactions is quite well understood. Many radiation-produced radicals can, however, possess excess energy ("hot radicals") which results in a high energy of activation. These

radicals can undergo reactions which do not normally occur. Also, the radiation-produced radicals can be formed in high concentrations in localized areas along the radiation track. This can result in product distributions considerably different from those expected in normal radical reactions.

Since analytical techniques are unable to distinguish between products formed from "hot radicals" and the products formed from "normal radicals" and also between those formed in localized high-concentration areas and those formed in more diffused radical-concentration areas, specific reaction rate constants derived from the analysis of products produced by an irradiation may or may not provide information regarding the actual radiolysis mechanisms. Such information would be enlightening as far as the overall degradation mechanism rates are concerned; however, it would leave completely obscure any detailed description of intermediate processes that occur. Any mechanism derived solely from kinetic considerations could very easily lead to erroneous mechanistic conclusions. Therefore, the most logical approach for ascertaining the mechanisms responsible for the observed chemical changes in an aromatic system is the non-kinetic approach combined with certain thermodynamic and kinetic considerations such as bond energies, radical reactivities and parameters which affect the nature of the radiation environment, i.e. dose, dose rate, LET, temperature, etc. Wherever possible a postulated reaction mechanism should be investigated independently of the radiation environment.

Before proceeding further into some aspects of free radical behavior and radiation kinetics, a brief summation of the foregoing discussion is in order. Radiation energy absorbed by an aromatic system results in the formation of excited molecules and free radicals which are responsible for the production of many of the yield products. These yield products can result from bond scissions, molecular rearrangement (or reactions involving the excited molecules and radical combination), radical attack reactions, or radical induced chain reactions of the radiolytically produced free radicals. The formation of the initial reactive species can be depicted by the following reactions:

$$A \xrightarrow{\quad\sim\sim\sim\quad} A^* \xrightarrow{\quad a\quad}$$
$$A \xrightarrow{\quad\sim\sim\sim\quad} A^+ + e \quad\longrightarrow\quad \text{radicals, rearrangement products, etc.}$$
$$A^+ + e \xrightarrow{\quad\quad} A^* \xrightarrow{\quad b\quad}$$

a = primary process
b = secondary process
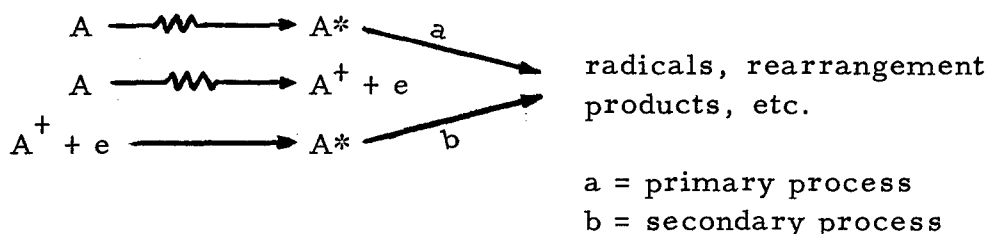
An electron produced by Compton scattering from 1 Mev. photon can result in the excitation of more than 30,000 molecules.[15] The energy of the 1 Mev. photon is in the order of 23×10^6 kcal./mole which is far in excess of chemical bond energies. These figures show that for Co^{60} gamma photons, which have energies of 1.17 and 1.33 Mev., if all the radiation energy were absorbed, very much damage to a molecule would result. Complete energy absorption does not occur and much of the energy absorbed by the molecule is dissipated by various processes without damage.

Free-radical reactions play important roles in many types of chemical reactions. The bond-fission responsible for radical formation (homolytic cleavage) can be depicted as: $A{:}B \longrightarrow A{\cdot} + B{\cdot}$ and is distinguished from heterolytic cleavage as thus: $A{:}B \longrightarrow A^- + B^+$. Energetically, homolytic cleavage should be favored over heterolytic cleavage. Often, however, solvent effects tend to promote the latter.[16] Generally, there are two classes of organic free radicals:

(a) those stabilized by resonance which possess a relatively long life such as triarylmethyls, and

(b) those not or only partially stabilized by resonance which are short lived, such as phenyl and methyl.

After a radical is formed in solution it can react in various ways depending upon the activity of the radical and the sensitivity of the solvent toward radical attack.[17] As seen in Table 1 the sensitivity of various aromatic compounds toward phenyl-radical attack varies considerably. Many radical reactions in aromatic systems may proceed through the formation of complexes which decompose or rearrange to form stable products. In the data it should be observed that ortho and para substitution in the aromatic solvent molecule predominates over meta substitution. This correlates with the expected resonance stabilization of the radicals.[24]

TABLE 1

RELATIVE REACTIVITY AND ISOMER DISTRIBUTION FOR THE
REACTION OF SOME AROMATIC COMPOUNDS WITH PHENYL
RADICALS DERIVED FROM BENZOYL PEROXIDE

Compound	Relative Reactivity	Isomer Distribution			Ref.
		% ortho	% meta	% para	
Benzene	1.00	--	--	--	
Anisole	1.2	67	18	15	18, 19
Toluene	1.9	71	17	12	20
Ethylbenzene	--	50	25	25	21
Biphenyl	4	48.5	23	28.5	22
Naphthalene	23.9	--	--	--	23

It has been suggested[25] that the formation of radicals by the decomposition of benzoyl peroxide in aromatic systems proceeds by one or more of the reactions indicated below ($R = \phi\cdot$ or $\phi COO\cdot$)*:
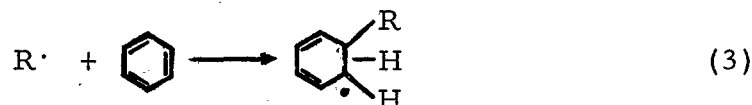
Reactions 1 and 2 are not probable since they would be endothermic. Reaction 3 parallels the reaction of halogens with benzene and the addition of methyl radicals to aromatic nuclei. The energetics involved in reaction 3 are not known. The path by which the product of reaction 3 is stabilized is conjectural; however, a disproportionation reaction 4 is plausible.

*These mechanisms are included here because of their similarity to later proposed mechanisms occurring in the radiolysis of diphenyl ether.

Another reaction (5) has also been postulated to account for the observed products.

       (5)
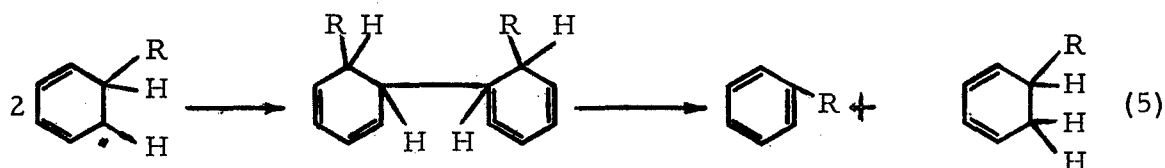
If, during irradiation, chemical bonds are to be broken, the weakest bonds should be the ones that are broken first and at a faster rate; this is observed indeed in the radiolysis of aliphatic hydrocarbons. For aromatic hydrocarbons, however, the effects of bond-energy differences are not so pronounced. If an aromatic molecule contains bonds other than C-C and C-H, then the energy of these bonds may be of significance in the radiolysis degradation mechanisms. In Table 2 are listed some of the commonly accepted energies for bonds which should be considered in the degradation of the aryl ethers. These data will be considered in greater detail in a later section.

TABLE 2

BOND ENERGY IN KCAL./MOLE (298.1°K)

Bond	Energy	Ref.
C-C (aromatic)	91	26
C=C (aliphatic)	146.4	26
C-C	80	26
C-O	85	26
O-H	110.5	26
=C-H	101.6	26
O-O (peroxide)	35	26
ϕ-H	105	27
ϕ-H	102	28
ϕ-OH	96	27
ϕ-OH	107	28

Predictions related to the magnitude of bond scissions occurring in a reaction based on bond energies alone should be made with caution since in free-radical reactions it is possible for Rice-Herzfeld mechanisms to occur.[29],[30] These mechanisms show how an experimental activation bond energy for a bond dissociation can be much less than the presumed dissociation energy for the bond.

Radiolysis of aliphatic liquid hydrocarbons results in the formation of rather larger quantities of gaseous products, considerable amounts of liquids of lower molecular weight and some polymeric material usually of a molecular weight in the order of the dimer.[31-35] Formation of these products has generally been attributed to the action of radiolytically produced free radicals which are stabilized by various radical-combination reactions and radical reactions with the target compound. The free-radical yield in the radiolysis of aliphatic hydrocarbons is in the region of $G^* = 6-9$.[36]

In the radiolysis of aromatic hydrocarbons the yield of free radicals is generally less than $G = 1$.[36] The yield of gaseous products is also very much reduced as compared to the gas yield from the aliphatic hydrocarbons. This indicates a greater stability of aromatic compounds toward radiolysis, especially with respect to scission reactions involving the aromatic ring. Aromatic compounds do not, however, show resistance to attack by free radicals, and as a result, form considerable amounts of polymeric material upon irradiation. The G-values for conversion of some aromatic hydrocarbons to polymers ($-G_m^{**}$) are listed in Table 3.[37]

TABLE 3

CONVERSION OF AROMATIC HYDROCARBONS TO POLYMERIC RESIDUES

Compound	$-G_m$
Benzene	0.75-0.98
Toluene	0.92-1.28
Polyphenyls	0.05-0.5

* The G value is the number of a species appearing or disappearing per 100 ev. of absorbed energy.

**-G_m will be used in this report to designate the number of target molecules disappearing per 100 ev. of energy absorbed.

The mechanism by which polymerization occurs is only speculative; however, arguments have been advanced supporting the following plausible reactions for benzene polymerization.[38, 39]

$$C_6H_6 \xrightarrow{\hspace{1cm}} C_6H_6* \longrightarrow C_6H_5 \cdot + H \cdot$$

$$C_6H_6 + H \cdot \longrightarrow C_6H_7 \cdot$$

$$C_6H_6* + R \cdot \longrightarrow RC_6H_6 \cdot \quad etc.$$
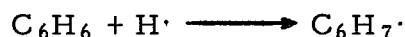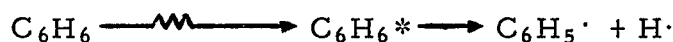
C_6H_6* = excited state benzene
R $\quad$ = H, C_6H_5 or C_6H_7

The above reaction sequence is important in showing that excited states of the target aromatic material may be involved directly in the polymer formation reactions.

The radiolysis of mixtures of aromatic compounds with other compounds has provided evidence for energy transfer phenomena. The hydrogen yield from the cyclohexane-benzene system has been studied extensively in these energy transfer phenomena.[32, 40, 41, 42] The presence of benzene (even in very small concentrations) in cyclohexane reduces considerably the formation of hydrogen during radiolysis. Energy absorbed by the cyclohexane is apparently transferred to the benzene in quantities sufficient to retard the formation of hydrogen from the cyclohexane. This transfer is known as the "sponge-type" protection.

The subject of energy transfer in radiation environments is only in its infancy and much is yet to be learned regarding the mechanisms by which the phenomenon occurs. Such mechanisms may, however, provide a basis for explaining such phenomena as decreased yield rates with increased doses during radiolysis. The formation of materials capable of receiving transferred energy without themselves being degraded may cause a reduction in the yield rate of initially formed radiolysis products. For example, most of the product G values from the radiolysis of cyclohexane decrease with increasing dose.[32] No information regarding the fate of the "protector" in such a system is known.

III. GENERAL RESEARCH APPROACH TO DIPHENYL ETHER DEGRADATION MECHANISMS

A. Introduction

With the preceding background related to changes observed during the radiolysis of an aromatic liquid, it would seem plausible that experiments from which a degradation mechanism is to be derived must yield the following information:

(a) identification of yield products and a quantitative measure of their concentration,

(b) parameters that would effect the rate of product formation or the type of products formed, such as dose, dose rate, sample size, temperature of irradiation, and effect of additives, etc., and

(c) identification of possible precursors to the individual yield products and a quantitative measure of the rate of intermediate formation. Where possible, the reactions of these intermediates should be studied in the absence of radiation.

In order to obtain usable data from experiments designed to give the above information considerable effort had to be devoted to the development of analytical techniques. A discussion of the more important analytical techniques used in this research program is given in Appendix A. The analytical methods investigated and/or used are listed below:

(a) gas chromatography (GC) - at column temperatures below 220°C.,

(b) high temperature gas chromatography (HTC) - at column temperatures above 220°C.,

(c) infrared spectroscopy (IR),

(d) ultraviolet spectroscopy (UV),

(e) visible spectroscopy,

(f) total acid titration,

(g) visible spectroscopy, (for total phenol)

(h) dilatometry,

(i)   countercurrent distribution (CCD),

(j)   micro molecular weight determination,

(k)   micro sublimation,

(l)   free-radical scavenging (using iodine and diphenylpicryl-hydrazil (DPPH),

(m) refractometry,

(n)   viscometry,

(o)   evaporation methods, (for total polymer)

(p)   column absorption chromatography,

(q)   color reactions and spot tests.

B.   Irradiation

A description of the Denver Research Institute Co^{60} source is given in Appendix B.   Source calibration methods are also included in this Appendix.   Unless otherwise noted in the tables of data, the dose rate for irradiations was about $5 \times 10^5 r./hr.$

C.   Chemicals

All the chemicals used in the radiolysis studies are listed in Appendix C.   Where available, the physical properties and purity of these compounds are also listed.

D.   Irradiation Technique

Most of the samples were prepared for irradiation in either 50 ml. or 2 ml. pyrex cells.   Unless otherwise stated the data in the tables were obtained from 2 ml. irradiated samples contained in 10 mm. O. D. cells.   The samples were deaerated by repeated freezing while under continuous pumping.

E.   General Analytical Technique

After irradiation the samples were subjected to the particular analysis most suited to ascertaining the objective of the experiment. The various concentrations of yield components were usually determined and calculated in terms of G values.

IV.   EXPERIMENTAL - RADIOLYSIS STUDIES OF DIPHENYL ETHER

A.   High Dose Irradiations of Diphenyl Ether

In order to ascertain the effects of radiation on diphenyl ether and to have sufficient quantities of the irradiated ether available for development of analytical methods, several ether samples were irradiated to rather high doses. These samples were analyzed by various methods to determine the quantity and nature of the yield products. Table 4 shows some of the gas chromatographic data obtained from these irradiations and the product identification derived from these data. The high-boiling yield products definitely identified by retention time comparison with authentic materials are:

(a)   o-diphenoxybenzene

(b)   m-diphenoxybenzene

(c)   p-diphenoxybenzene

(d)   4-biphenylyl phenyl ether

(e)   bis m- phenoxyphenyl ether

(f)   bis p-phenoxyphenyl ether

Two other components were tentatively identified as o- and p-phenoxyphenol.

Yield products boiling lower than diphenyl ether were hydrogen, a small amount of carbon monoxide, benzene and phenol.

Table 5 lists the yield values calculated from the gas chromatographic analysis of a typical high-dose irradiated sample. Calculations from these data show that, based on the total amount of diphenyl ether destroyed by the radiolysis, only a little more than 10% of the destroyed ether can be accounted for in the yield products detectable by gas chromatography. These data indicate that a great part of the degraded ether goes to form polymeric material of molecular weight greater than 358; this corresponds to the molecular weight of a bis[phenoxyphenyl] ether. The fact that considerable polymeric material is formed can be observed in Figure 1 and also Table 6, which show the relation of viscosity change for diphenyl ether to dose of irradiation. The relation of the viscosity change at 100°F. to the change of 210°F. indicates that the radiation-formed polymer must have a rather high ASTM viscosity slope which is

TABLE 4

IDENTIFICATION OF KNOWN MIXTURES AND DIPHENYL ETHER RADIOLYSIS PRODUCTS BY GAS CHROMATOGRAPHY USING DIFFERENT COLUMNS AT HIGH TEMPERATURES

Retention Time in Seconds for Various Gas Chromatographic Columns

Component	7 ft. 20% polyphenyl ether Column, Temp. 318°C.		7 ft. 20% polyethylene Column, Temp. 294°C.			7 ft. 0.25% polyethylene on NaCl Column, Temp. 265°C.		
	Known Mixture	Irrad. Ether[a]	Known Mixture	Irrad. Ether[a]	Irrad. Ether[b]	Known Mixture	Irrad. Ether[b]	Irrad. Ether[a]
Diphenyl ether	50	50	60	60	60	45	45	45
o-Terphenyl		150c 250c		130c 220c	125c	85		
o-Diphenoxybenzene	315	300	515	520	520	120	115	115
m-Diphenoxybenzene	400	405	850	860	870	160	150	155
p-Diphenoxybenzene	460	470	930	930	950	180	175	170
m-Terphenyl		540d				180	200d	200d
p-Terphenyl						230		
Bis(m-phenoxyphenyl) ether	1920	1880	1840	1830	1830	370	360	355
Bis(p-phenoxyphenyl) ether	2760	2600	2650	2600	2580	490	480	470

a. Diphenyl ether irradiated to 0.755×10^{22} (100 ev) at 100°C., 50 ml. samples.
b. Diphenyl ether irradiated to 1.37×10^{22} (100 ev) at 29°C., 50 ml. samples.
c. Detected radiolysis components tentatively identified as o- and p-phenoxyphenol.
d. This peak identified in subsequent analysis as 4-Biphenylyl phenyl ether.

TABLE 5

THE ANALYSIS OF AN IRRADIATED DIPHENYL ETHER

Component	G Value[a]	g. $\times 10^3$	wt. % of total ether	wt. % of destroyed ether
Diphenyl ether[b]	-0.727	2811.0	6.49	100.00
Hydrogen	.0041	--	--	--
Carbon monoxide	.0006	--	--	--
Benzene	.036	18.95	.044	0.67
Phenol	.200	126.6	.292	4.50
o-Phenoxyphenol	.0215	24.62	.057	0.88
p-Phenoxyphenol	.0124	14.20	.033	0.51
o-Diphenoxybenzene	.0403	66.66	1.54	2.37
m-Diphenoxybenzene	.0165	27.20	.063	0.97
4-Biphenylyl phenyl ether[c]	.0082	13.6	.031	0.48

a. Number of molecules of component produced or destroyed per 100 ev. energy absorbed.

b. Diphenyl ether irradiated to a dose of 1.37×10^{22} 100 ev.

c. This component also contains p-diphenoxybenzene.
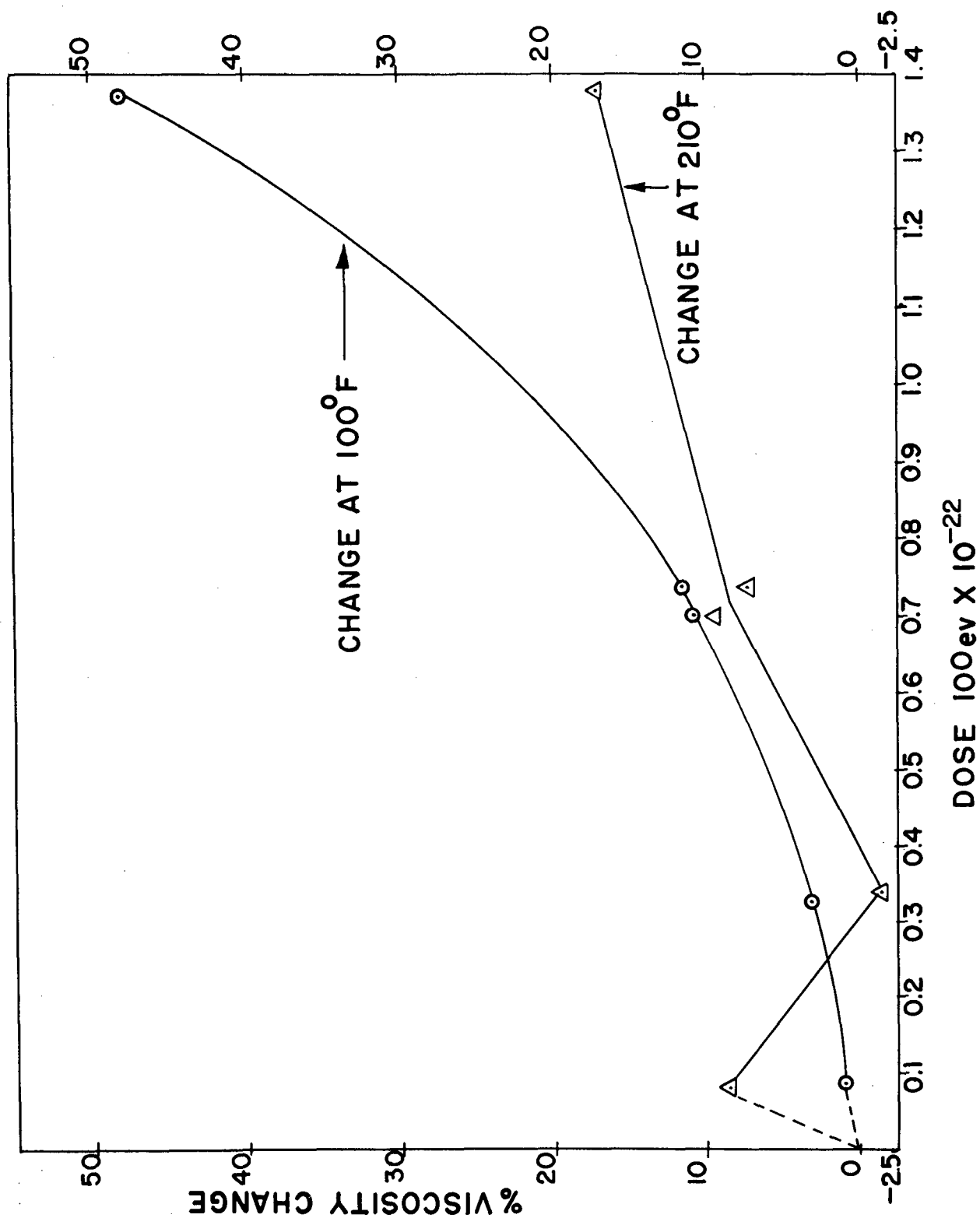
Figure 1. Relation of Viscosity Change in Diphenyl Ether to Total Radiation Dose.

TABLE 6

DATA FROM IRRADIATED DIPHENYL ETHER

Dose								
$r \times 10^{-8}$		3.18	3.23	3.23	6.56	1.32	0.327	3.16[a]
$100 \text{ ev} \times 10^{-22}$		0.70	0.747	0.860	1.37	0.325	0.077	0.755
n_D^{20}	Before	1.5796	1.5796	1.5796	1.5796	1.5796	1.5796	1.5796
	After	1.5817	1.5817	1.5815	1.5836	1.5838	1.5829	1.5850
Viscosity change (%)	100°F	10.5	10.9	11.5	47.2	2.9	1.5	12.1
	210°F	9.4	7.2	5.1	14.8	-1.8	8.0	11.3
Yield Values	G_{gas}	--	0.0014	0.0106	0.066	0.0061	--	0.0151
	G_{H_2}	--	0.0014	0.009	0.066	0.0061	--	0.011
	$G_{Benzene}$	0.056	0.039	0.042	0.039	0.023	0.046	0.076
	G_{Phenol}	0.277	0.195	0.240	0.141	0.160	0.415	0.377
	$-G_m$	0.83	0.86	0.86	0.73	2.4	2.15	1.53

a. Irradiated at 100°C.

characteristic of the aryl ethers and aromatic hydrocarbons.[3] This polymer, when removed from both the solvent and most of the relatively low-boiling irradiation products is a glassy brown solid at room temperature. A fraction of the polymeric material, separated on an absorption column, was found to have a number average molecular weight of 17,000.

Several attempts were made to fractionate the high-dose irradiated ether in order to characterize the yield products not detectable by gas chromatographic techniques. Investigations of readily available solvent systems applicable to countercurrent distribution separations did not indicate a probability of fractionating the radiation-produced polymer. Column absorption chromatography did accomplish some separation although no distinct fractions were obtained. Table 7 describes the collected fractions after solvent evaporation and infrared examination.

It is apparent from these observations that all fractions are mixtures of compounds of varying molecular structures. A portion of the combined fractions 82-114 and 221-247 was placed in a high temperature gas chromatograph at 320°C. column temperature. The fact that no components were detected indicated (a) thermal decomposition of the sample, (b) insufficient quantity of a particular component for detection, or (c) the presence of an extremely high-boiling material equal to or larger than a five phenyl ether. Of these, (c) appeared to be the most probable.

A portion of the 82-114 fraction was placed in a micro-sublimation apparatus similar to that described by Melhuish.[43] A helium flow of about 10 ml./min. was maintained in the apparatus. The material did not move from the hot zone at 320°C. The temperature of the hot zone was then raised to 420°C. At this temperature a small amount of material moved down the column; the remainder did not move and partially charred after one hour in the apparatus. This again indicated a very high-boiling material of relatively high molecular weight.

The fraction 221-247 contained a material that readily sublimed from the bulk of the fraction. This material, a white solid, was very probably p-phenylphenol. It gave the same color reactions as p-phenylphenol and melts sharply at 162°C. (uncorr.) p-phenylphenol melted at 165°C.

The total weak-acid concentration of this irradiated ether was determined by the non-aqueous titration methods described by Cundiff and Marcunas.[44] A value of 1.32×10^{-4} equivalents of weak acid per

TABLE 7

CHROMATOGRAPHIC SEPARATION FRACTIONS
OF IRRADIATED DIPHENYL ETHER

Fractions Combined	Appearance	Molecular Structures Present as Determined by Infrared Spectroscopy
1 - 20	Yellow fluorescence	Diphenyl ether
21 - 42	Yellow fluorescence	Diphenyl ether and small amount Aliphatic material
43 - 53	Green fluorescence	As above
54 - 64	Yellow fluorescence	As above
65 - 69	Blue fluorescence	As above with indications of cyclic aliphatic
70 - 81	Blue fluorescence	Ether, aliphatic, 1:4-aromatic substitution, traces of OH, C=O and C≡C; no CH_3 or 1:3-aromatic substitution
82 - 114	Yellow fluorescence Yellow glass	Ether, increased aliphatic, strong 1:3-aromatic substitution
115 - 138	Yellow fluorescence Brown very viscous oil	As above with $(CH_2)_4$ and CH_3, C=O, and C≡C
139 - 220	Brown viscous oil	As above
221 - 247	Brown viscous oil, phenolic odor when hot	Aromatic ether, 1:4-aromatic substitution some 1:3-aromatic substitution, OH

gram of irradiated ether was found. If this were all phenol it would be equivalent to 1.22% phenol in the ether. Gas chromatography indicated 0.57% (wt.) of the irradiated ether to be phenol. The remainder of the weakly acidic constituents must be higher molecular weight phenols, such as the p-phenylphenol, o- and p-phenoxyphenols, and other acidic materials which were indicated in the infrared spectra of the chromatographed fractions.

A rather extensive spectral examination of an unfractionated irradiated diphenyl ether was made. The types of molecular changes observed as the result of irradiation are presented below. The changes are very similar to those observed in the column-fractionated irradiated diphenyl ether (see Table 7).

The infrared differential spectrum of diphenyl ether and the irradiated ether exhibits difference bands for hydroxyl (3700 cm^{-1}), aromatic and aliphatic hydrogen (3050 and 2950 cm^{-1}). This spectrum and those of the pure and irradiated diphenyl ether are given in Figure 2.

Phenol was identified by gas chromatography and presence of phenolic compounds was confirmed by the OH stretch and by the OH deformation at 1360 cm^{-1},[45] which are the strongest of the observed difference bands.

Aliphatic compounds were indicated by the CH stretch, and deformations at 2950 and 1465 cm^{-1}. Some confirmation existed around 1400 and at 730 cm^{-1}, though these bands were very weak.

Olefinic bonds absorb weakly at about 1650 and 965 cm^{-1}, though the spectrum is too weak for positive identification.

The region from 1580 to 1800 cm^{-1} possessed a number of overlapping bands, one or more of which could be due to carbonyl; the assignments in this region must be regarded as inconclusive.

Difference bands at 1160, 1140, 1065, 1030 cm^{-1} might be ascribed to differences in aromatic structures due to such compounds as benzene or to such phenomena as polymerization of the parent compound to one or more dimer, trimer, or higher polymeric groups of compounds. The band at 860 cm^{-1} may indicate para-substituted phenyl nuclei, indicating linking of phenyl groups of the parent compound at the para position into polymer chains.
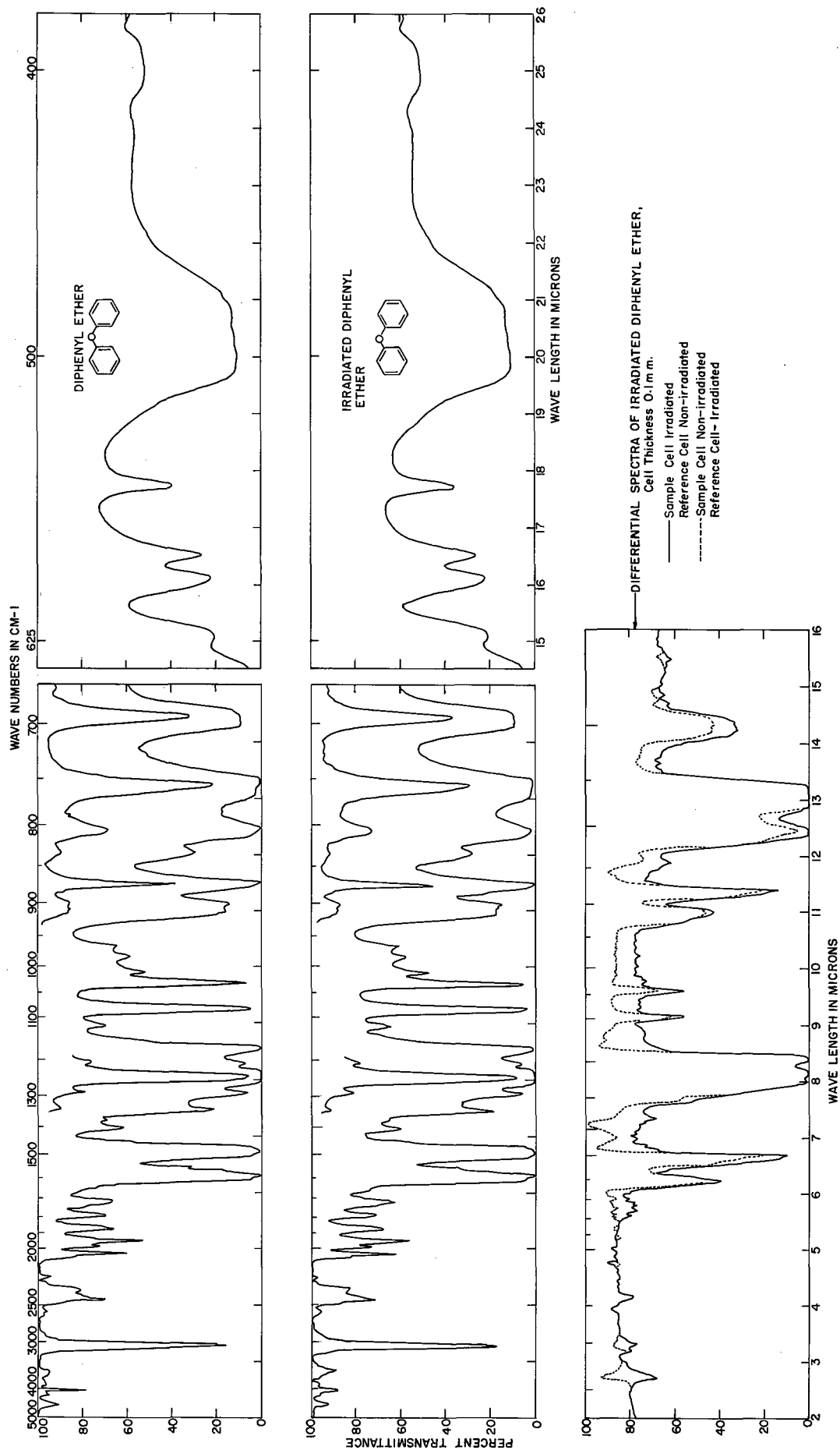
Figure 2. Infrared Spectra of Irradiated and Pure Diphenyl Ether.

Strongest of the difference bands in the near-infrared region occur at 2.88, 2.82, 2.12, and 1.44 microns as shown in Figure 3. The first two are due to free- and associated-hydroxyl-hydrogen-stretching vibrations and the band at 1.44 microns is the first overtone of the free-OH stretching mode. One can therefore suspect the presence of phenolic and/or alcoholic compounds.

The remaining difference bands show the presence of aromatic hydrogen, and most important aliphatic hydrogen (confirmed in the infrared) including methyl, methylene, and olefinic hydrogen. This suggests the rupture of some of the aromatic rings, forming both saturated and unsaturated fragments.

It was desirable to eliminate those difference bands due to compounds already identified in the irradiated diphenyl ether. Phenol had been identified by gas chromatography; therefore, a synthetic mixture of phenol in diphenyl ether was prepared and a differential spectrum recorded as shown in Figure 4. As a result of this spectrum one can attribute for the difference bands at 3.00, 2.88, 2.82, 2.12, 2.05, 1.99, 1.94, 1.90, and 1.44 microns to phenol. These are indicated by the small letters "ph" on the differential spectrum of the irradiated diphenyl ether in Figure 3. Calculation of the phenol concentration in irradiated diphenyl ether from the synthetic mixture gave a phenol content of 0.8% which compared favorably with the 0.9% found by gas-chromatographic methods for this ether sample.

It is of interest to note that dilute phenol solutions in non-polar solvents show major OH absorptions at 1.42, 2.76, and 2.85 microns (7050, 3622, and 3514 cm^{-1}), the latter two being free- and associated-hydrogen stretching modes. However, when phenol is dissolved in diphenyl ether, these bands shift to lower frequencies, 6940, 3546, and 3472 cm^{-1} respectively, indicating hydrogen bonding between the phenol and diphenyl ether rather than bonding between phenol molecules.

The above spectral investigations concerning the partially fractionated ether and the ether direct from irradiation are significant as they show that the radiolysis of diphenyl ether causes some cleavage or saturation of the aromatic rings to form molecular fragments of aliphatic character and trace amounts of carbonyl structures. Of greater significance, however, was the observation that 1:3 and 1:4 aromatic substitution had occurred during radiolysis and this was interpreted to indicate that the polymeric material formed was predominantly meta and para substituted.
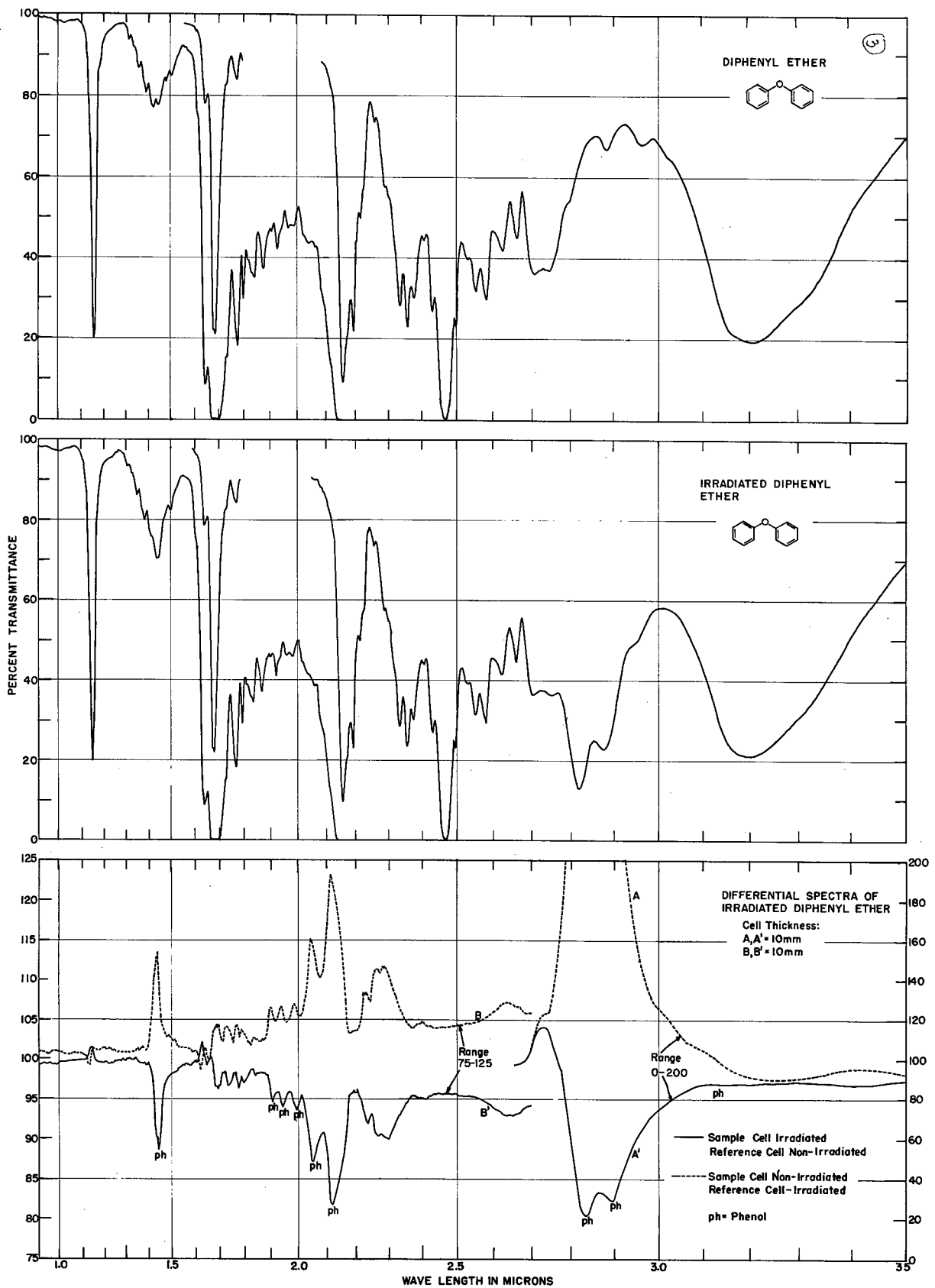
Figure 3.   Near Infrared Spectra of Irradiated and Pure Diphenyl Ether.
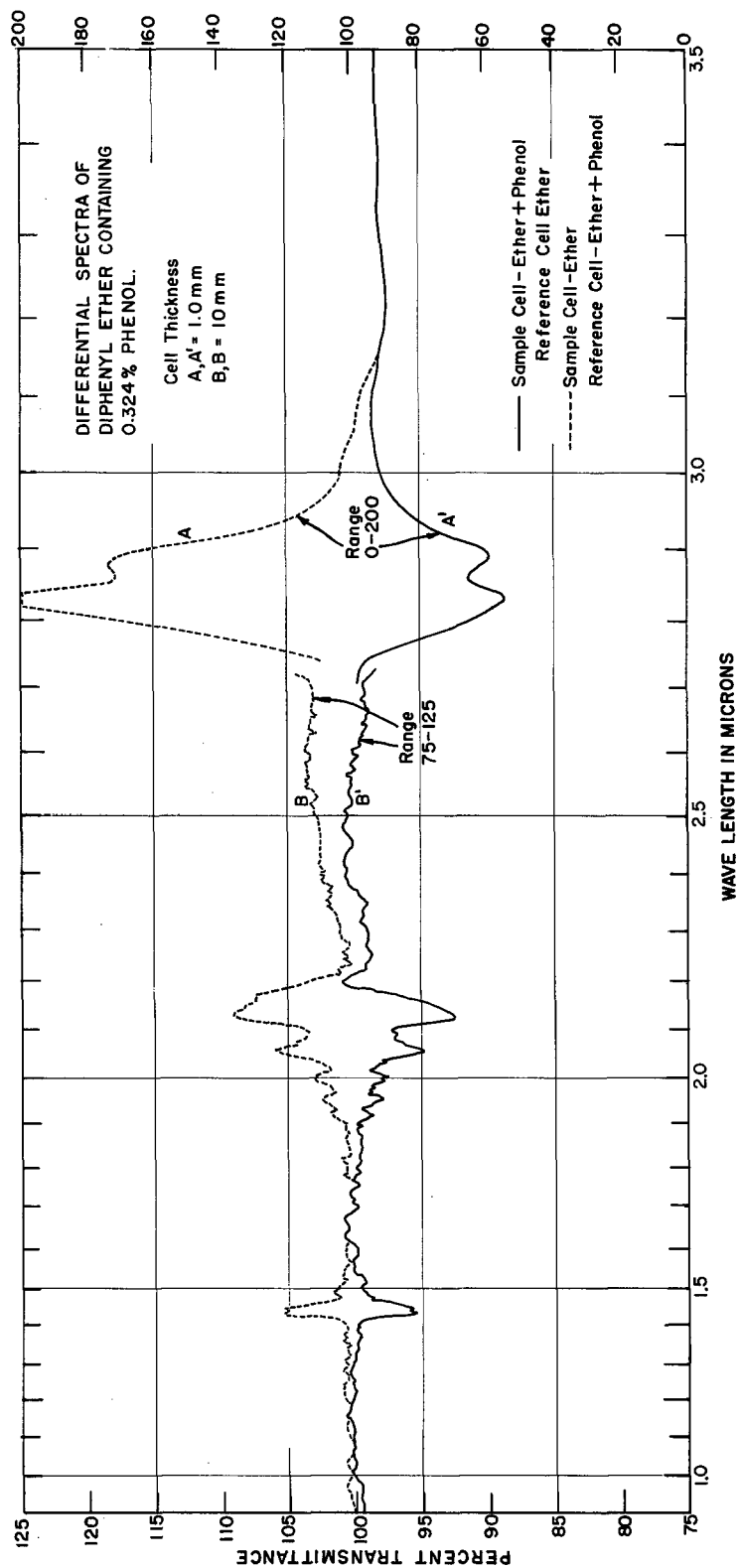
Figure 4.   Differential Spectra of Diphenyl Ether Containing Phenol

Further observations regarding the nature of the polymeric material and its yield will be included in subsequent sections.

B.   Establishment of Dose Ranges for Radiolysis Mechanism Studies

In order to determine the mechanisms by which a material is degraded during radiolysis the investigations should be conducted at absorbed doses as low as is feasible analytically. Higher radiation doses increase the concentration of yield products and as the concentration increases these yield products may enter into reactions competing with the primary degradation steps. In the irradiations of diphenyl ether to high doses, rather significant changes in viscosity were observed (Figure 1) and these changes were attributed to the formation of polymeric materials. The formation of these materials should be detectable as changes in the density of the ether during radiolysis. Consequently a sensitive dilatometer was constructed (see Appendix A) and relative changes in the density of the diphenyl ether during radiolysis were observed. The results of this study are shown in Figure 5. It would be expected that reactions in which a greater number of molecules are formed than the number originally present in the dilatometer (scission reactions) would cause a decrease in density or an increase in the volume required to contain the material. Polymerization reactions would cause the opposite effect. The data plotted in Figure 5, therefore, can be interpreted as follows:

(a) At absorbed doses up to 30×10^{18} 100 ev. (A-B) the predominant effect is a decrease in the solution density which must result from scission reactions.

(b) At doses greater than 80×10^{18} 100 ev. (C-D) the density of the solution increases rapidly, showing that a polymerization reaction is occurring and is affecting the solution density at a much greater rate than the scission reactions.

(c) In the intermediate dose range (B-C) the scission and polymerization reactions must be occurring simultaneously and at such competing rates as to have very little overall effect on the density of the solution.

It was found that gas chromatography can detect and quantitatively measure the formation of benzene and phenol at absorbed doses less than 30×10^{18} 100 ev. Since the effects of cell geometry and sample volume on the rate of product formation were not known and since the analytical
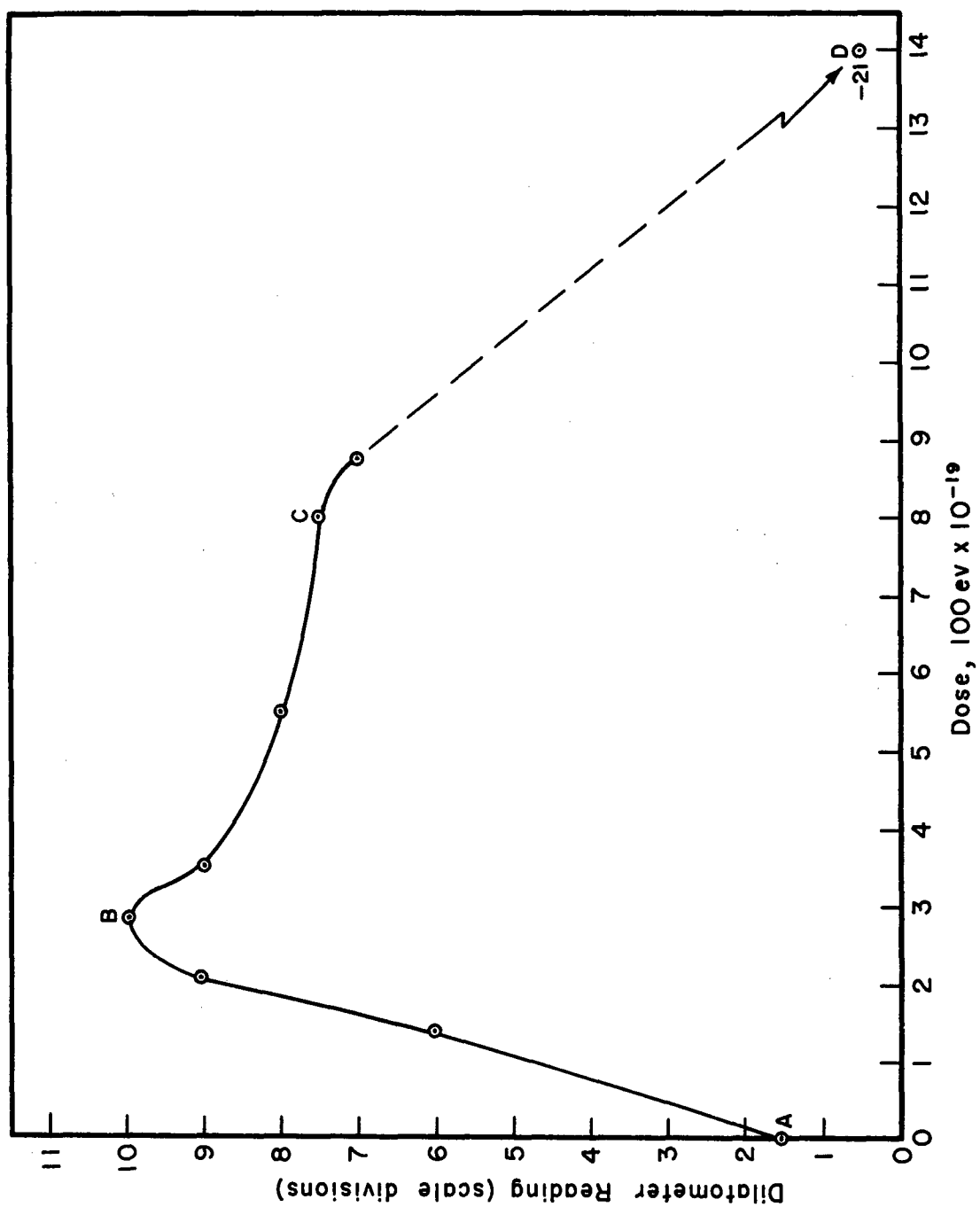
Figure 5. Dilatometer Studies of Diphenyl Ether

techniques were sufficiently sensitive for product analysis, it was arbitrarily decided to consider absorbed doses of 20×10^{18} 100 ev. or less to be the low dose region and to assume that in this region only scission reactions were occurring predominantly. It is known, however, that polymerization is also occurring in this dose region, but it is not considered to be the major reaction (see later sections). Absorbed doses in the region of $20\text{-}80 \times 10^{18}$ 100 ev. were considered intermediate doses and any dose greater than this range was classed as a high-dose irradiation.

C.   Low-Dose Irradiations of Diphenyl Ether

Since the primary degradation processes are most likely to occur in the low-dose region without significant interference from competing reactions of yield products, several parameters that might affect the degradation mechanism were investigated. To study the possible effects of varying parameters on the radiolysis mechanisms it was decided to use the yield of phenol as a measure of these effects. The physical parameters that would most likely affect the radiolysis mechanisms or reaction rates are sample size, dose rate and temperature of irradiation. Experiments to ascertain these affects are described below.

1.   Effect of Sample Size on Phenol Yield

The Denver Research Institute Co^{60} source has a region of about two inches in height in which the radiation flux is quite uniform. If one maintains the sample height constant and varies the sample diameter, the effective path length of an irradiation track can be varied. Several irradiations were made in sealed vials with 0.5 and 1.0 cm. diameters which when filled to equal heights contained 1.0 and 4.0 ml. respectively. These samples were irradiated to equal doses (not equal times) and the phenol concentration was determined by gas chromatography. The data plotted in Figure 6 show that the rate of phenol formation increases with sample thickness. The slope of curve A (the thicker sample) is 0.213 which is equal to G_{Phenol}. For curve B the slope is 0.168. The total number of phenol molecules formed is also greater in the thicker sample thus indicating that increasing the radiation track length increases the amount of phenol produced per unit of absorbed energy. This is indicative also that the processes responsible for initiation of phenol formation mechanisms must occur in or very near the radiation track.

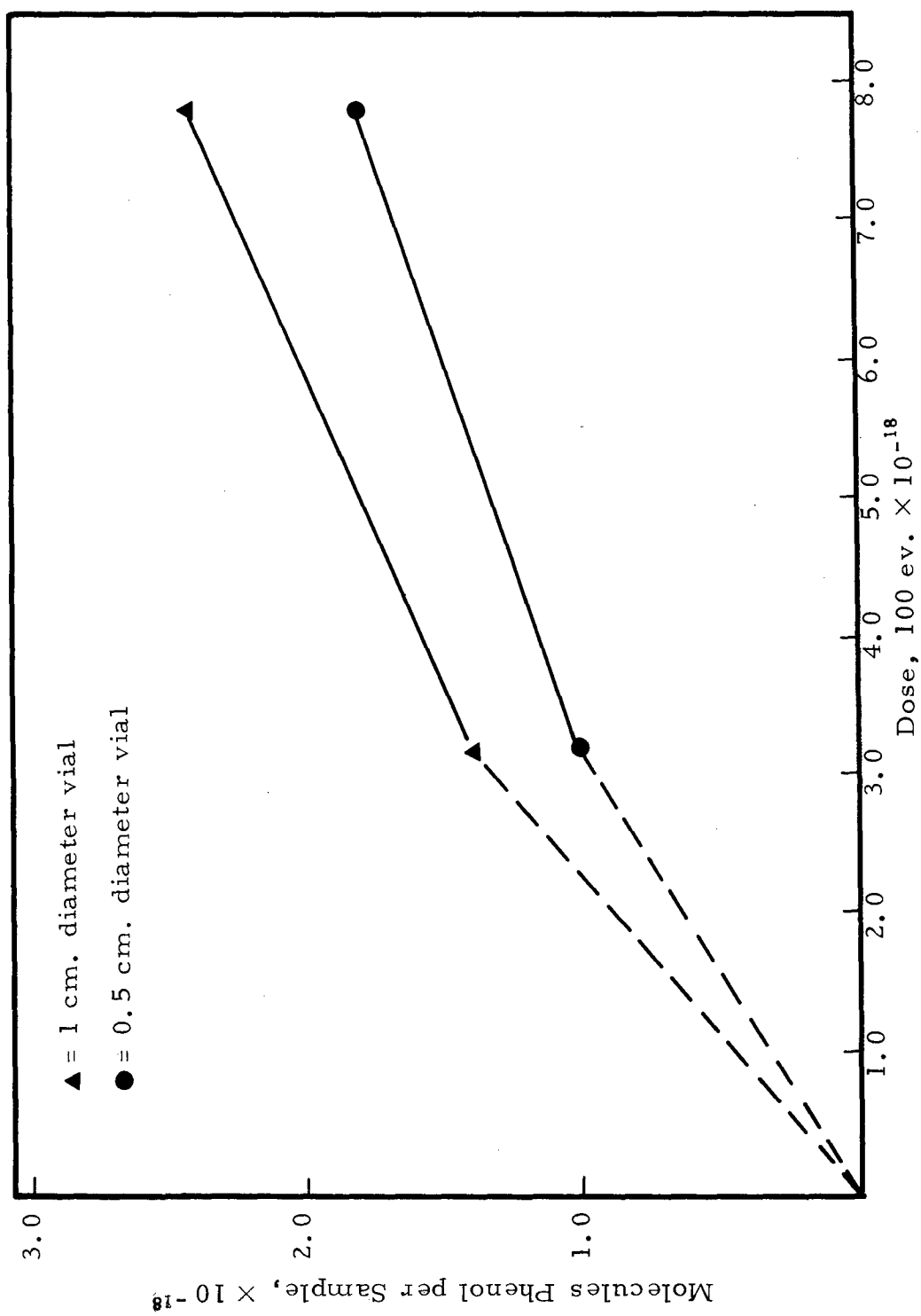Figure 6. The Effect of Sample Size on the Formation of Phenol in Diphenyl Ether.

2.   Effect of Dose Rate on Phenol Yield

Several irradiations of diphenyl ether to nearly equivalent total doses, but at irradiation rates of 5.2×10^5 r. per hour and 1.6×10^5 r. per hour, were made. The phenol concentration was determined by gas chromatography and by spectrophotometry. The data from these analyses are plotted in Figure 7. Curves A and B (the higher dose-rate curves) are of particular interest and significance. It was established that both analytical methods give the same result in determining the phenol concentration in diphenyl ether solutions containing known amounts of phenol. Since the spectrophotometric analysis of the irradiated ethers will measure the total phenolic hydroxyl concentration and the gas chromatographic analysis determines only the phenol concentration, the differences in concentration exhibited by curves A and B must be due to phenolic materials other than phenol. These data, therefore, indicate that phenolic materials other than phenol are being produced in the ether in irradiations made at a high-dose rate. The data obtained from the low-dose rate irradiations (curves C and D, Figure 7), though more randomly scattered, tend to show similar phenolic concentrations and approach than those exhibited by curve B. This leads to the conclusion that, if the difference in curves A and B are due to phenolic materials other than phenol, then low-dose rate irradiations tend to reduce the reactions by which the phenolic materials (other than phenol) are formed.

A logarithmic plot of curves A and B (Figure 7), as shown in Figure 8, indicates that the rate of formation of phenol and that of the total phenolic materials seems to be first order in the $2-6 \times 10^{18}$ 100 ev. region. The rate of phenol formation appears to approach the rate of total phenolic material formation. This would indicate that reactions other than those responsible for the phenolic material formation are consuming, at an increasingly greater rate, the radicals needed for the phenolic material formation. This is further indicated by the fact that at slightly higher doses, detectable amounts of diphenoxybenzenes are found in the irradiated ethers.

3.   Effect of Temperature on Phenol Yield

Low-dose irradiations of diphenyl ether were made at 50-80°C. The phenol and phenolic material concentrations were determined by gas chromatography and by spectrophotometry. The data from these analyses are plotted in Figure 9 and show that the yield of phenol is nearly independent of the temperature of irradiation. The yield of phenolic materials
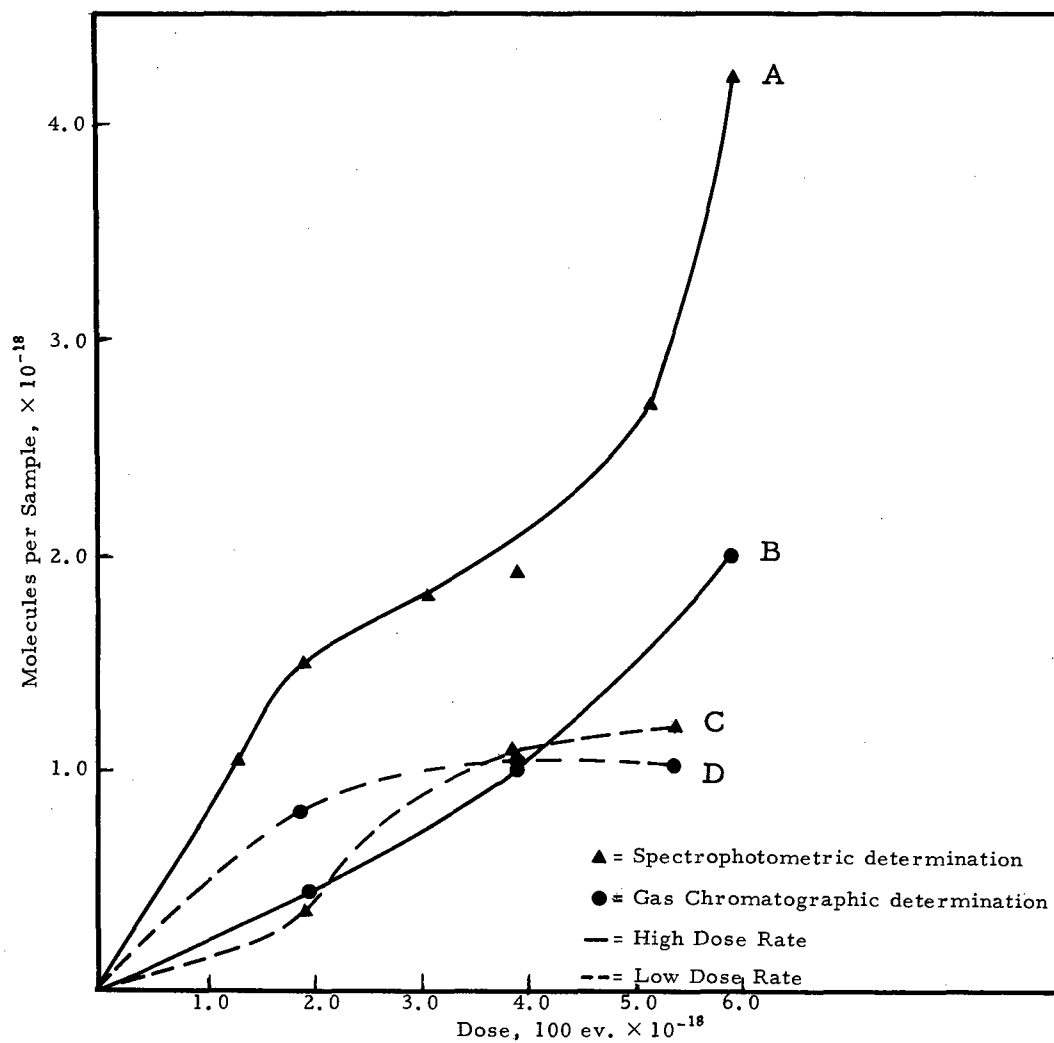
Figure 7. The Effect of Dose Rate on the Formation of Phenol and Phenolic Materials in Diphenyl Ether.
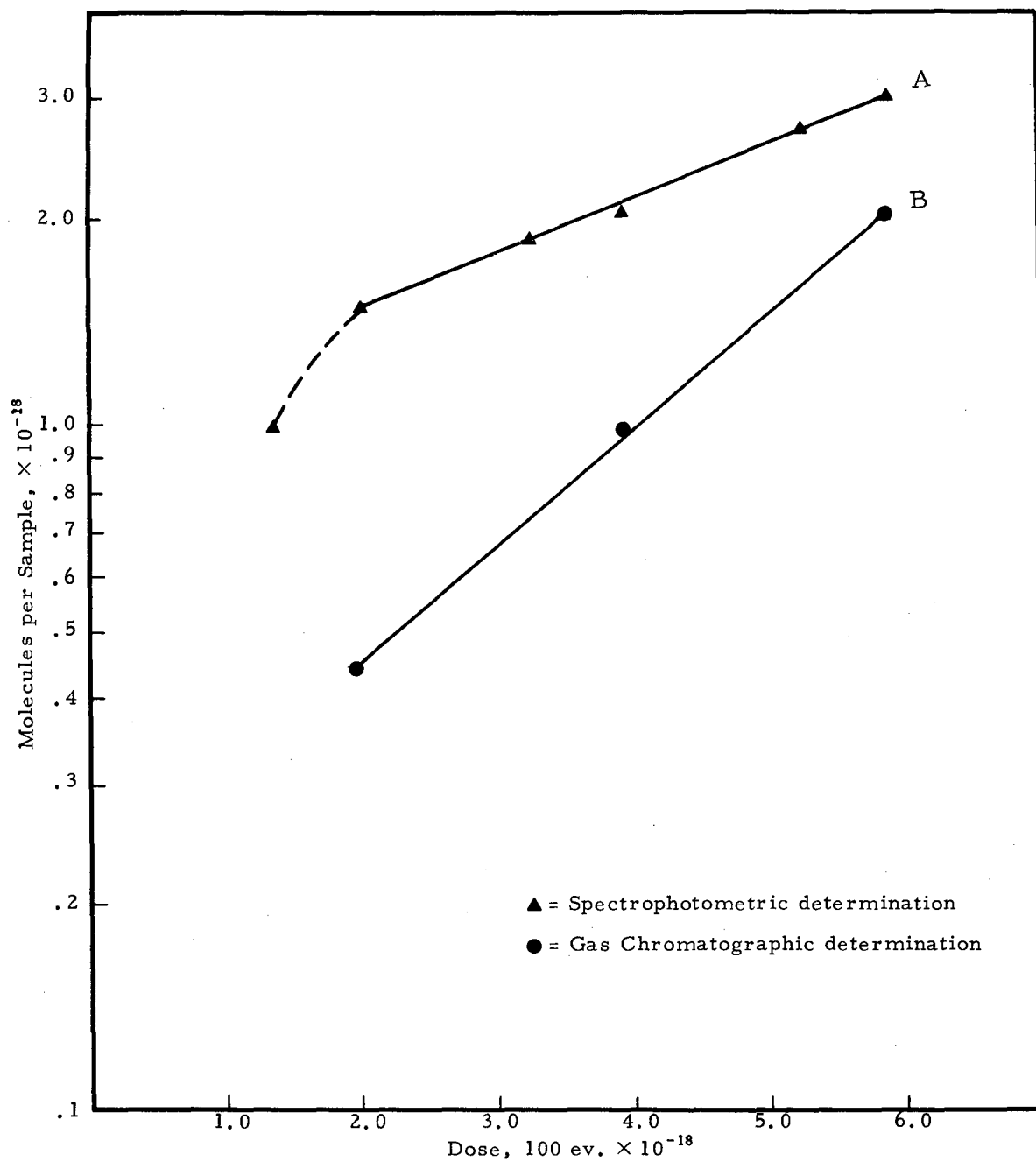
Figure 8.   The Effect of High-Intensity Dose Rate on the Rate of Formation of Phenol and Phenolic Materials in Diphenyl Ether.
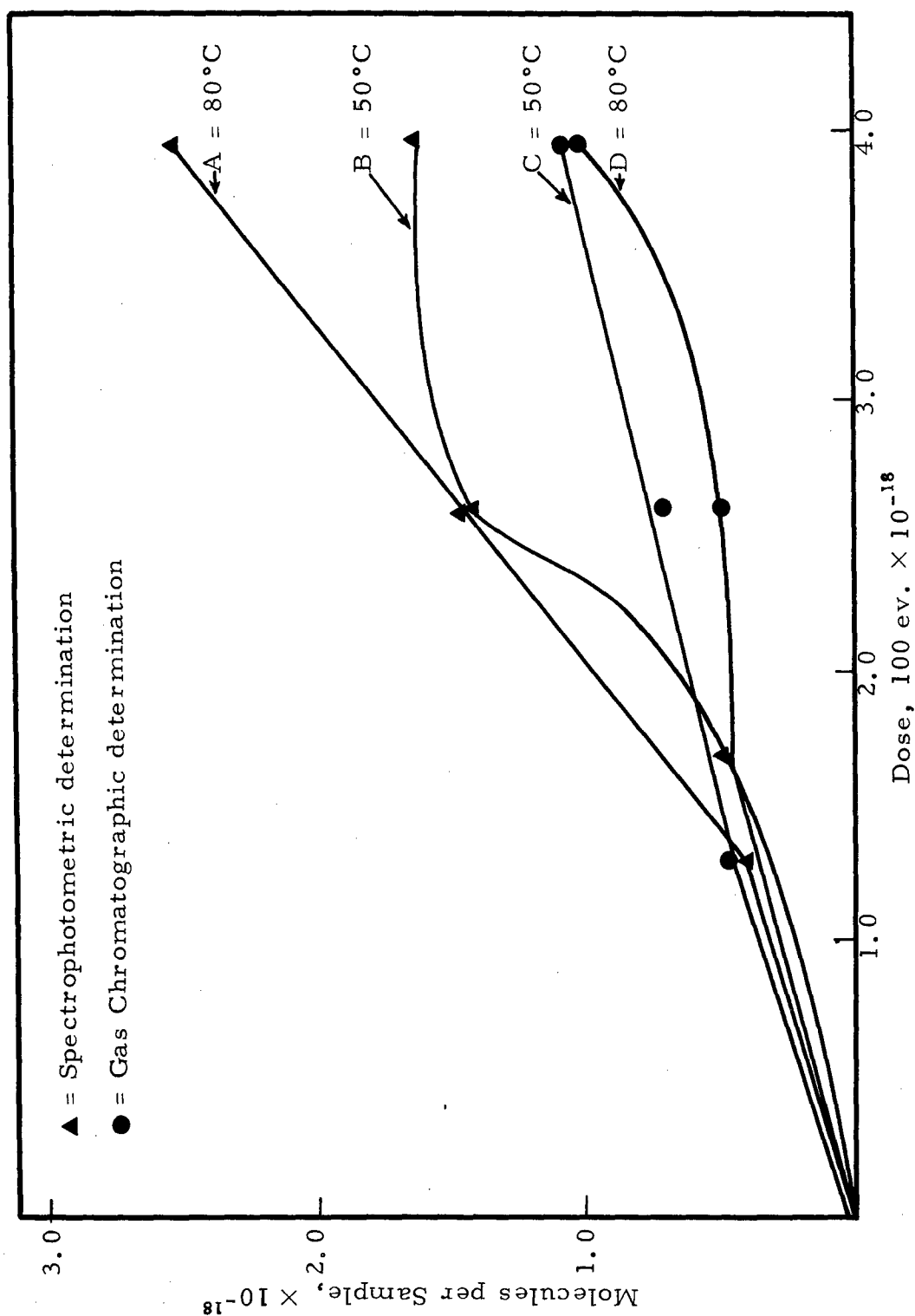
Figure 9. The Effect of Temperature on the Rate of Formation of Phenol and Phenolic Materials in Diphenyl Ether.

is, however, dependent on the temperature of irradiation. Since an increase in temperature will increase the rate of radical diffusion, it would appear that the formation of the phenolic material (not phenol) is a function of the rate of radical diffusion in the irradiated ether. This contention can be further verified by the observations (as discussed in the previous section) that the phenolic material yield is greater at higher dose rates where radical formation and diffusion rates must be greater. These data again indicate that the processes responsible for phenol formation must occur in the immediate vicinity of the radiation track and are not dependent upon diffusion from this area or from the solvent cage.

The results of the above experiments have shown that variation of dose rate, sample size and temperature of irradiation can cause changes in the type of yield products and the rate of product formation. Therefore, all subsequent irradiations (except where specifically noted) concerned with studying the degradation mechanisms of diphenyl ether were made at the higher dose rate using 2 ml. samples of the ether contained in 10 mm. O. D. pyrex cells at an ambient source temperature of 26°C.

D.   Experiments Concerned with Ascertaining the Primary Degradation Mechanisms in the Radiolysis of Diphenyl Ether

Based on the types of yield products detected and identified from the radiolysis of diphenyl ether (Section IV A) and the theoretical probability of free-radical formation (Section II) it would be reasonable to assume that most of the observed changes could be the result of free-radical formation and subsequent radical reactions.

The data shown in Table 8 is a compilation of the analytical results obtained from the radiolysis of standard samples of diphenyl ether at irradiations ranging from low to high doses. Experiments designed to elucidate the radiolysis mechanism must lead to a reasonable interpretation of the following observations drawn from these data:

(a)   The yield of phenol is always five to seven times greater than the benzene yield. If the formation of these two components resulted directly from cleavage of the ether (C-O) bond with the formation of phenyl and phenoxy radicals, then one would expect the yield of phenol and benzene to be more nearly equal. Since this is not observed, it must be assumed that the reactions involved in the formation of these components is more complex than a simple hydrogen atom abstraction reaction by the radicals.

TABLE 8

ANALYTICAL DATA FROM THE RADIOLYSIS OF DIPHENYL ETHER

	Yield Component Analyzed																	
	Benzene	Phenol	Hydrogen	Benzene	Phenol	Hydrogen	Benzene	Phenol	Hydrogen	Benzene	Phenol	Hydrogen	Benzene	Phenol	Hydrogen	Benzene	Phenol	Hydrogen
Mean Dose* 100 ev.×10⁻¹⁸	3.76	3.76	3.76	14.8	14.8	14.8	47.6	47.6	47.6	83.6	83.6	83.6	109.6	109.6	109.6	176.7	176.7	176.7
Mean G value	.0368	.2169	---	.0433	.2795	.0015	.0433	.2381	.0024	.0488	.2647	.0032	.0393	.2420	.0038	.0425	.2433	.0045
Phenol: Benzene ratio		5.9			6.4			5.5			5.4			6.2			5.7	
δ	.0132	.0690	---	.010	.032	---	.016	.0294	---	.0049	.0236	---	.0043	.0235	---	.0026	.0182	---
N	7	23	---	13	13	---	14	14	---	9	9	---	13	13	---	6	6	---
V_δ (%)	35.8	31.8	---	23.1	11.4	---	36.9	12.34	---	10.0	8.9	---	10.9	9.7	---	6.1	7.5	---
Molecules of component per molecule of ether × 10⁴	.182	1.08	---	.845	5.46	.029	2.72	14.9	.151	5.38	29.2	.353	5.68	35.0	.549	9.91	56.7	1.049
$-G_m$		---			---			---			3.0			1.40			.41	
$G_{polymer}$		---			.175			.375			.43			.44			.45	

* Mean dose received by the ether

δ Standard deviation

N Number of samples analyzed

V_δ Relative standard deviation (see Ref. 46)

(b)   The apparent disappearance of diphenyl ether ($-G_m$) is greater at lower doses than at higher doses. While accuracy of determining the $-G_m$ at lower doses is considerably less than that at the higher dose determinations these data indicate that the rate of ether disappearance does decrease at higher absorbed doses.

(c)   The rate of polymer formation increases with increasing dose.

The following experiments describe the approach utilized to arrive at some interpretations of the above observations. Particular emphasis was placed on the mode of free-radical reaction as related to phenol formation.

1.   Determination of Free-Radical Formation and Yield

Considerable work has been done in the past to determine the free-radical yields in the radiolysis of organic liquids. Methods such as radical-initiated polymerization reactions,[47] iodine scavenging[35,48] and diphenylpicrylhydrazyl (DPPH) scavenging[48,49] have been studied extensively. The use of polymerization reactions as a means of measuring free-radical yields was eliminated from consideration in this study because the method is not very sensitive and to be utilized effectively, considerable knowledge of the reaction kinetics for the system has to be known. The use of iodine for a radical scavenger was found to be undesirable since absorption bands of the diphenyl ether and yield products interfered with the iodine absorption band measurements required to determine the iodine concentration.

In proper concentrations, diphenylpicrylhydrazyl (DPPH) acts as a suitable free-radical scavenger. Figure 10 shows the effect of radiation on solutions of DPPH in diphenyl ether. The non-linearity of curves 1-4 (higher concentrations of DPPH) is probably due to the DPPH not following the true zero-order kinetics required for ideal radical scavenging.

Curve 5 is the result of several analyses of DPPH solutions ranging in concentration from 3.2×10^{-3} to 6.48×10^{-3} molar. In this concentration region the DPPH is acting as a scavenger with no observable effects of radiolytic and temperature deterioration.

The slope of curve 5 (Figure 10) is equal to the rate of disappearance of DPPH which in turn is a measure of the rate of formation
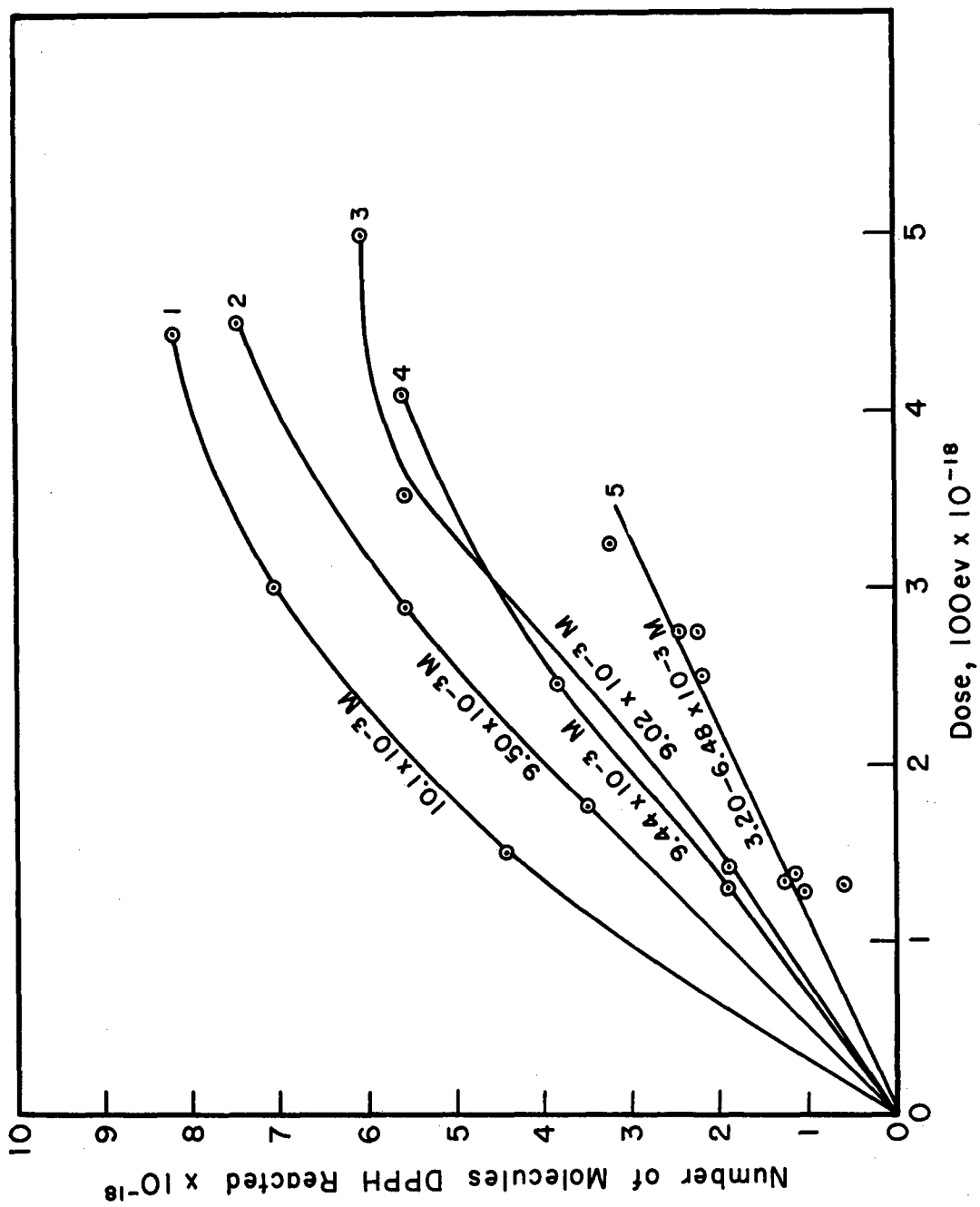
Figure 10. Effect of Radiation on Solutions of Diphenylpicrylhydrazyl in Diphenyl Ether.

of free radicals. This rate is 0.94 radicals per 100 ev. of energy absorbed ($-G_{DPPH} = 0.94$).

Radical scavenger studies with DPPH were made at 30° and 40°C. The curves in Figure 11 show the effect of temperature on the radical yield. The difference in slope of the two curves in their most linear portion gives a yield value of 0.046 radicals per 100 ev. per °C. This value may be high since the stability of DPPH is affected to a certain extent by increasing temperature, however, the data show that either the rate of radical formation is greater at the higher temperature or there is an increase in the rate of radical diffusion from the immediate area of formation to a point where more efficient scavenging can occur.

Irradiation of DPPH solutions at dose rates of 5.2×10^5 r./hr. and 1.7×10^5 r./hr. showed no change in yield of free radicals thus indicating that the rate of radical formation by scavenger measurements is independent of dose rate.

2. The Action of Phenol, Phenolic Compounds, and Polyaryl Ethers on the Radiolysis of Diphenyl Ether

Since the destruction rate of diphenyl ether decreases as the total absorbed dose is increased (see Table 8), , it was desirable to determine the effects of some of the radiation yield products on the initial yield of such components as phenol and other phenolic compounds.

Samples of diphenyl ether containing 0.017 M concentrations of phenol were irradiated to varying doses up to 100×10^{18} 100 ev. (high-dose region). The irradiated solutions were analyzed by gas chromatography for phenol content. It was found that the amount of phenol present was increased only by an amount equivalent to that expected if there had been no phenol present in the original ether. This indicates that phenol, present as an additive or as a yield product has no detectable effect on further formation of phenol during radiolysis. The yield of benzene was increased slightly by the presence of phenol in the high dose irradiations.

Other ether solutions containing equivalent quantities of o-, m-, and p-diphenoxybenzene, 4-biphenylyl phenyl ether, o-, m-, and p-phenoxyphenol and biphenyl were irradiated to low doses and analyzed by gas chromatography for phenol and by spectrophotometry for total phenolic material. All solutions showed no significant change in
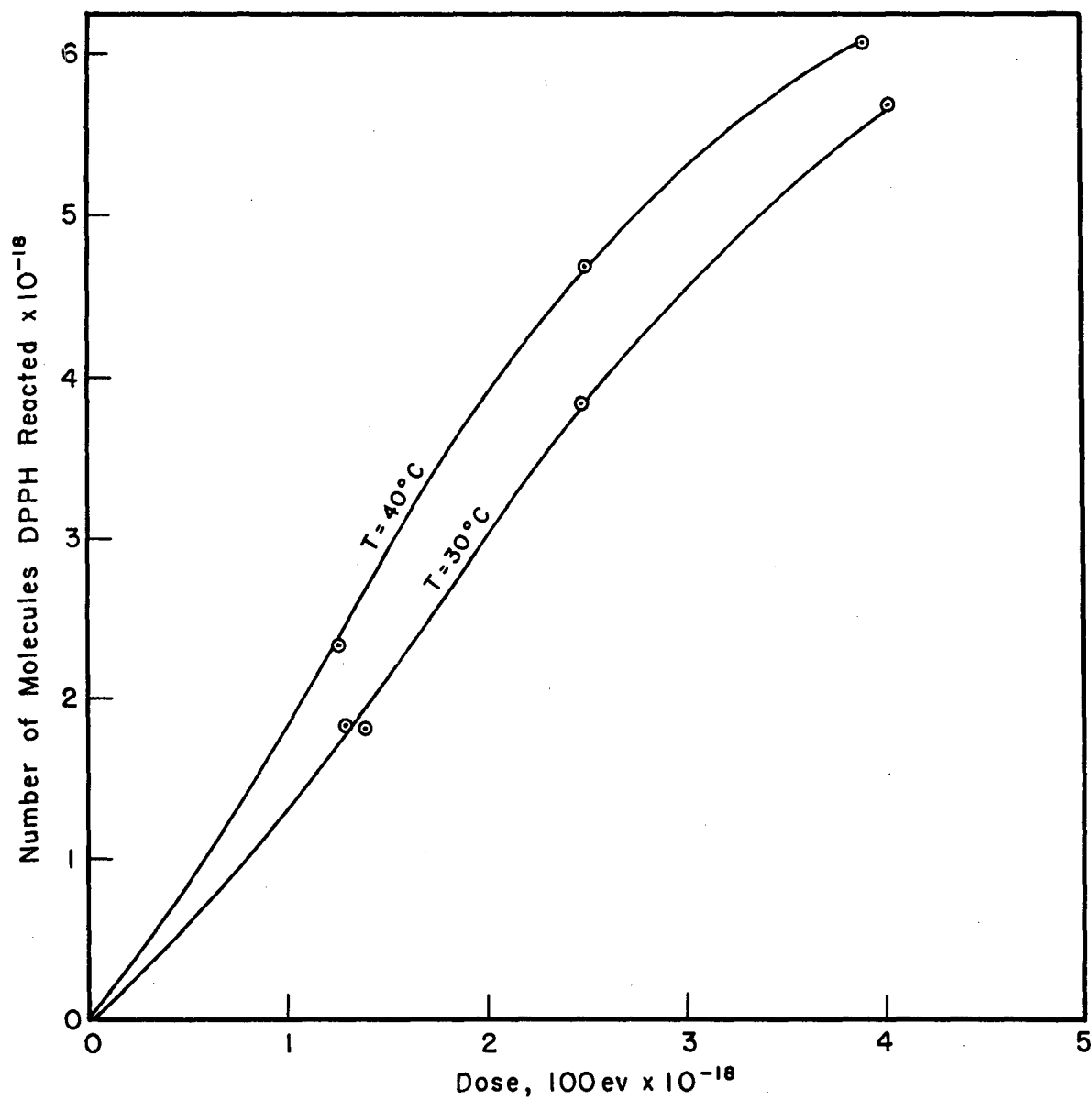
Figure 11. Effect of Temperature on the Radical Yield in
Diphenylpicrylhydrazyl-Diphenyl Ether Solutions.

phenol yield and no increase in benzene yield. The aryl ethers had no effect on the yield of total phenolic material. However, the presence of polyarylphenols in the irradiated solutions reduced to a small degree the yield of total phenolic material.

3.   Energy Transfer in Organic Systems

Considerable work has been done in the past regarding the protective action imparted to a solvent by small amounts of a solute. Most of the work has been concerned with the hydrogen yield from the irradiation of cyclohexane containing small amounts of benzene.[32, 40, 41, 42] In this system it has been shown that the hydrogen yield is reduced very significantly from that expected if there were no interaction between the solvent and solute. In general, the reduction in hydrogen yield is attributed to a transfer of absorbed energy from the solvent molecules to the protector or solute molecules in such a manner as to prevent the normal degradation of the solvent.

It is known in the radiolysis of diphenyl ether that, as the absorbed dose is increased, the yield values of certain components vary and this variation may be the result of certain "energy transfer" characteristics of some of the components being formed during the radiolysis. It was, therefore, of interest to make a survey of the effects of solutes other than benzene on the hydrogen yield from cyclohexane and thus ascertain in a relative manner the degree of protection certain components might impart in the radiolysis of diphenyl ether. It was decided to determine these effects at rather low doses in order to minimize the effects of any secondary reactions that might occur.

The data plotted in Figure 12 were obtained from the radiolysis of solutions of cyclohexane containing varying amounts of aromatic solutes irradiated to doses of about 10×10^{18} 100 ev. The electron fraction of a component was calculated as described by Manion and Burton.[41] This fraction is not, however, significantly different from a volume fraction calculation for the components studied. In Figure 12, line A represents the hydrogen yield expected if there were no interaction between the components. The data show that benzene is quite effective in reducing the hydrogen yield and this reduction is generally attributed to energy transfer or energy absorption phenomena. In the perspective of this interpretation, the aryl ethers must be considered to be more efficient energy absorbers than benzene. Certain phenols may be even more efficient.

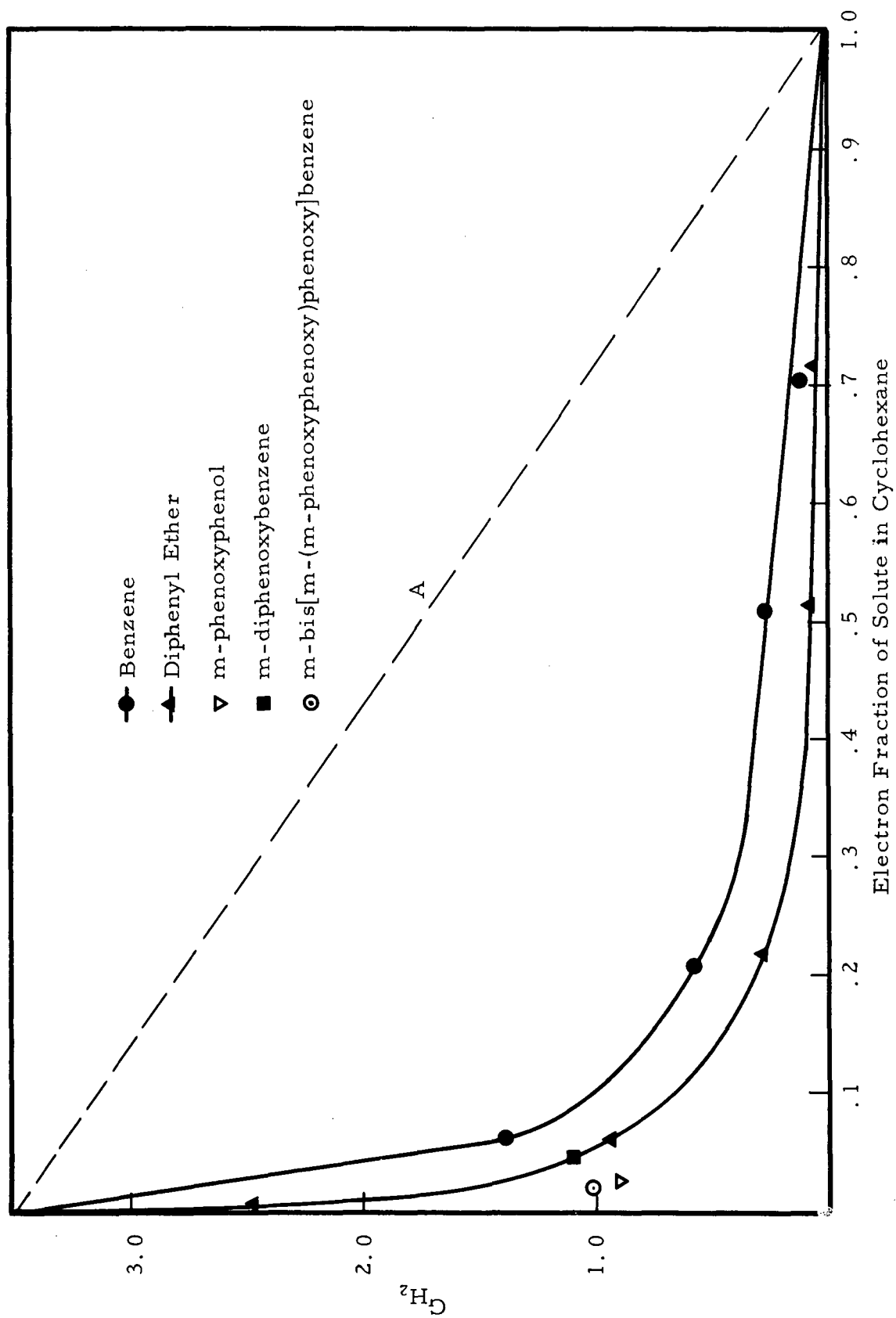Figure 12. Effect of Aromatic Compounds on the Hydrogen Yield of Cyclohexane.

Legend:
- ● Benzene
- ◄ Diphenyl Ether
- ▽ m-phenoxyphenol
- ■ m-diphenoxybenzene
- ⊙ m-bis[m-(m-phenoxyphenoxy)phenoxy]benzene

x-axis: Electron Fraction of Solute in Cyclohexane

y-axis: G_{H_2}

The primary significance of this data is that it shows that classes of compounds similar to those found in the radiolysis of diphenyl ether are capable of protecting a system from apparent radiolytic degradation. It is reasonable to assume that such compounds when formed during diphenyl ether radiolysis could subsequently impart a protective effect to the ether and thus cause the appearance of near constant ratios between the yield products from the ether when irradiated to high doses.

There is evidence, however, to indicate that the protective action imparted to cyclohexane by the aryl ethers is done so at a sacrifice to the stability of the ether. This could shed some doubts on the assumption that the protective role of the solute is acting via a true energy transfer mechanism. The evidence that the ether degradation rate is increased as a result of radiolysis in cyclohexane is born out by the following: After radiolysis, the cyclohexane from a sample containing diphenyl ether and a sample containing m-diphenoxybenzene was removed and the resulting residue analyzed by gas chromatography. Although the analysis was not made on an absolute quantitative basis, it was estimated that the phenol concentration in the diphenyl ether sample was increased about two to four fold over that expected if there had been no interaction between the solution components. From the sample containing m-diphenoxybenzene, a similar increase in the yield of phenol and diphenyl ether was observed. If this increased degradation of the ether is related to a transfer of energy from the solvent to the solute, then the energy is being transferred at a fast enough rate to protect the degradation of the solvent but too fast for the solute to dissipate the energy before degradation. Another, and a more plausible explanation for the increased solute degradation is the action of free radicals on the decomposition of the ether solute. The following section shows that the action of phenyl radicals produced in the absence of radiation in diphenyl ether causes the formation of many compounds similar to those found as the products from the radiolysis of diphenyl ether.

4. The Action of Phenyl Radicals on Diphenyl Ether

The thermal decomposition of benzoyl peroxide is known to be a good source of phenyl and benzoyl radicals.[50] In solution, dismutation of the benzoyl radicals leads to the formation of carbon dioxide and phenyl

radicals. Considerable work has been done concerning the rate of benzoyl peroxide decomposition in various solvents. Very little work has been done, however, regarding the identification of the reaction products, particularly in aryl ether solutions.

Since the initial radiolysis reactions of diphenyl ether have been presumed to be a cleavage of the carbon-oxygen bond to form phenyl and phenoxy radicals, it was thought that the formation of phenyl radicals from benzoyl peroxide decomposition would provide a good means of ascertaining the role of the phenyl radical in the radiolytic degradation of diphenyl ether. A series of exploratory experiments were made to determine the nature of the products formed by the thermal decomposition of benzoyl peroxide in diphenyl ether.

The following compounds, identified by gas chromatographic methods, were found to be produced in diphenyl ether as the result of the thermal decomposition of benzoyl peroxide:

    (a) Benzene

    (b) Phenol

    (c) o, m, p-Diphenoxybenzene

    (d) 4-Biphenylyl phenyl ether

    (e) Bis(m-phenoxyphenyl) ether

    (f) Bis(p-phenoxyphenyl) ether

Although gas chromatographic methods do not provide a positive means of component identification when working with unknown mixtures, the similarity of the chromatogram obtained from the peroxide decomposition to that obtained from the radiolytic decomposition of diphenyl ether is great enough to preclude any doubt of the identity of the above compounds. An additional major component found in the peroxide decomposition has been tentatively identified as phenyl benzoate.

These exploratory experiments were very significant in providing clues concerning the fate and mode of reaction of phenyl radicals in diphenyl ether. To further elucidate the role of the phenyl radical in the formation of products other experiments were made. In Figure 13 is shown the relation of benzene to phenol formation that resulted from the thermal decomposition at 75°C. of diphenyl ether solutions containing 2% benzoyl peroxide. It is seen that benzene and phenol are produced
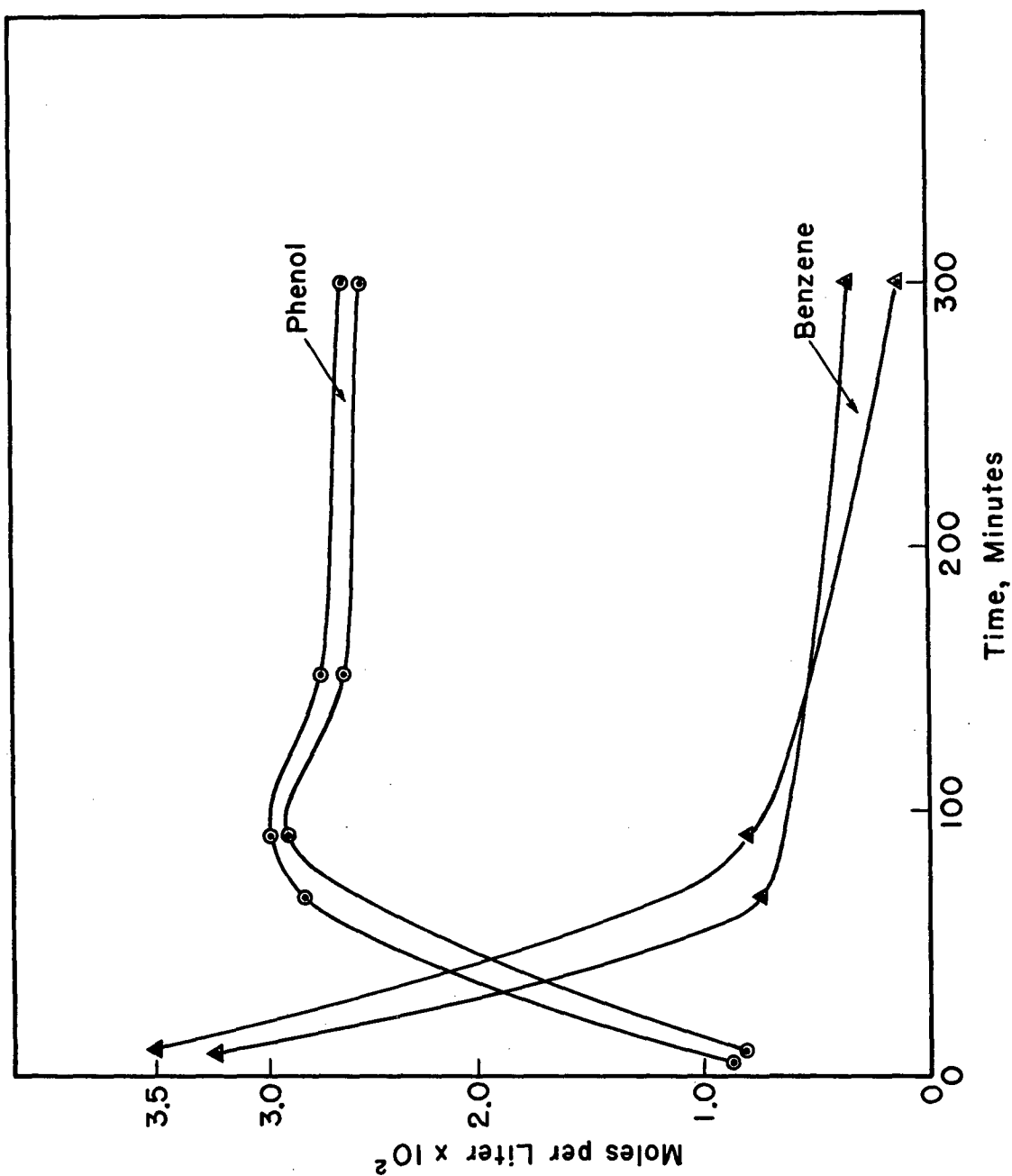
Figure 13. The Relation of Benzene and Phenol Formation from the Thermal Decomposition of Benzoyl Peroxide in Diphenyl Ether.

almost spontaneously with the original benzene concentration being much greater than the phenol concentration. As the decomposition proceeds, the phenol concentration increases as the benzene decreases.

After five-hours' reaction it was determined by gas chromatography that about 12% of the ether had been consumed. The components (c) to (f) (page 43) were formed only in very small quantities initially and gradually increased in concentration as the reaction proceeded.

It was of interest to determine whether the formation of phenyl radicals and their subsequent reactions in diphenyl ether were accompanied by the formation of hydrogen. An evacuated benzoyl peroxide-ether solution was thermally decomposed in a sealed tube and after reaction for two hours at 70°C. the atmosphere above the reaction solution was sampled and analyzed for hydrogen. The analysis showed no evidence of hydrogen formation.

Samples of diphenyl ether containing 0.1% benzoyl peroxide were irradiated and analyzed for benzene and phenol. The yield values from these irradiations and those of similar irradiations without the peroxide are shown in Table 9.

TABLE 9

BENZENE AND PHENOL YIELDS FROM THE RADIOLYSIS
OF DIPHENYL ETHER AND DIPHENYL ETHER CONTAINING
0.1% BENZOYL PEROXIDE

Composition Irradiated	Dose, 100 ev. $\times 10^{-18}$	$G_{Benzene}$	G_{Phenol}
Diphenyl ether	31	.035	.241
Diphenyl ether and peroxide	31	.040	.444
Diphenyl ether	62	.052	.261
Diphenyl ether and peroxide	62	.055	.354

These data show that the presence of the peroxide in the irradiated mixture increases the yield of phenol significantly but has only a minor effect on the benzene yield. It is not known how the peroxide decomposes under irradiation but the peroxide band is weak (Table 2) and

a reasonable assumption would be that the radiolytic decomposition of the peroxide would not differ greatly from the thermal decomposition. The increased phenol yield from the irradiation of diphenyl ether in the presence of peroxide indicates that the precursor to phenol formation is the phenyl radical.

5.   The Action of Phenyl Radicals in Other Aromatic Systems

To establish definitely that the phenol from the above decompositions was not being formed from some kind of degradation through rearrangement of the benzoyl peroxide, a sample of the peroxide was decomposed thermally in benzene and the resulting solution analyzed for phenol. No phenol was found. Since no phenol was found this experiment would indicate that the phenyl radical is the precursor to phenol formation.

It was of interest to determine the effects of the phenyl radical on other compounds similar in structure to diphenyl ether. Small amounts of benzoyl peroxide were decomposed thermally in the following solvents: diphenylmethane, diphenylamine and bis(3-methylphenyl) ether. If the action of the phenyl radical in these solvents were to proceed similarly to that in diphenyl ether, then one would expect to find toluene, aniline, and m-cresol, respectively, in the reaction products. Gas chromatographic analysis of the reaction products showed that these expected compounds were formed.

6.   The Action of Phenoxy Radicals

If the initial radiolytic degradation of diphenyl ether forms the phenyl radical, presumably an equal quantity of the phenoxy radical would be formed. A search of the chemical literature revealed no clear and unambiguous way of forming the phenoxy radical in solution and in the absence of radiation. It has been indicated, however, that a benzoyl-peroxide thermal decomposition in solution with a small amount of phenol present will result in the formation of some phenoxy radicals along with other expected radicals.[51]

To ascertain the possibility that the phenoxy radical can be formed by the above method, a sample of benzene containing a small amount of benzoyl peroxide and phenol was heated for one hour at 70°C. Gas chromatographic analysis of the reaction mixture showed that some diphenyl ether had been formed. The presence of an ether in this reaction mixture was

confirmed by infrared spectroscopy. This information was interpreted to indicate that phenoxy radicals had been formed and that the diphenyl ether formation resulted either from the combination of the phenoxy and phenyl radicals or from the reaction of the phenoxy radical with benzene.

When the phenol-peroxide decomposition was made in diphenyl ether products similar to those formed in the absence of phenol were found. This was to be expected since the reaction forms predominantly phenyl radicals and the phenoxy radicals to a lesser extent. Of particular interest, however, was a change in the ratio of the products p-diphenoxybenzene and 4-biphenylyl phenyl ether. From diphenyl ether, decomposed either radiolytically or by phenol-peroxide, p-diphenoxybenzene is formed in greater quantities than 4-biphenylyl phenyl ether. In the peroxide-decomposed ether (no phenol added) 4-biphenylyl phenyl ether is formed in greater quantities than p-diphenoxybenzene. This indicates that the phenoxy radical is formed by the presence of phenol in the peroxide decomposition and indicates the type of compounds this radical is responsible in forming.

These observations indicate that the phenoxy radical is responsible in forming (in diphenyl ether solution) the high-boiling products identified as ethers in which each phenyl group is separated by an oxygen linkage. The reaction of the phenyl radical is associated with the formation of high-boiling compounds composed of a phenyl radical attached directly to another phenyl group.

7. Hydrogen Yield from the Radiolysis of Diphenyl Ether

The amount of hydrogen formed during the radiolysis of diphenyl ether is quite small. The hydrogen-yield data plotted in Figure 14 indicates that the yield gradually increases and appears to become constant at a value of $G_{H_2} = 0.005$. It is believed, however, that the hydrogen yield probably is constant over the entire irradiation dose range and a true value for this yield would be more nearly $G_{H_2} = 0.005-0.006$. The analytical methods for the determination of hydrogen did not permit the detection of all the hydrogen (see Appendix) that might have been present in a dissolved state. The uncertainty of the quantity of dissolved hydrogen in low- and medium-dose irradiations would make any conclusions regarding the increasing rate of formation in this dose region rather dubious.
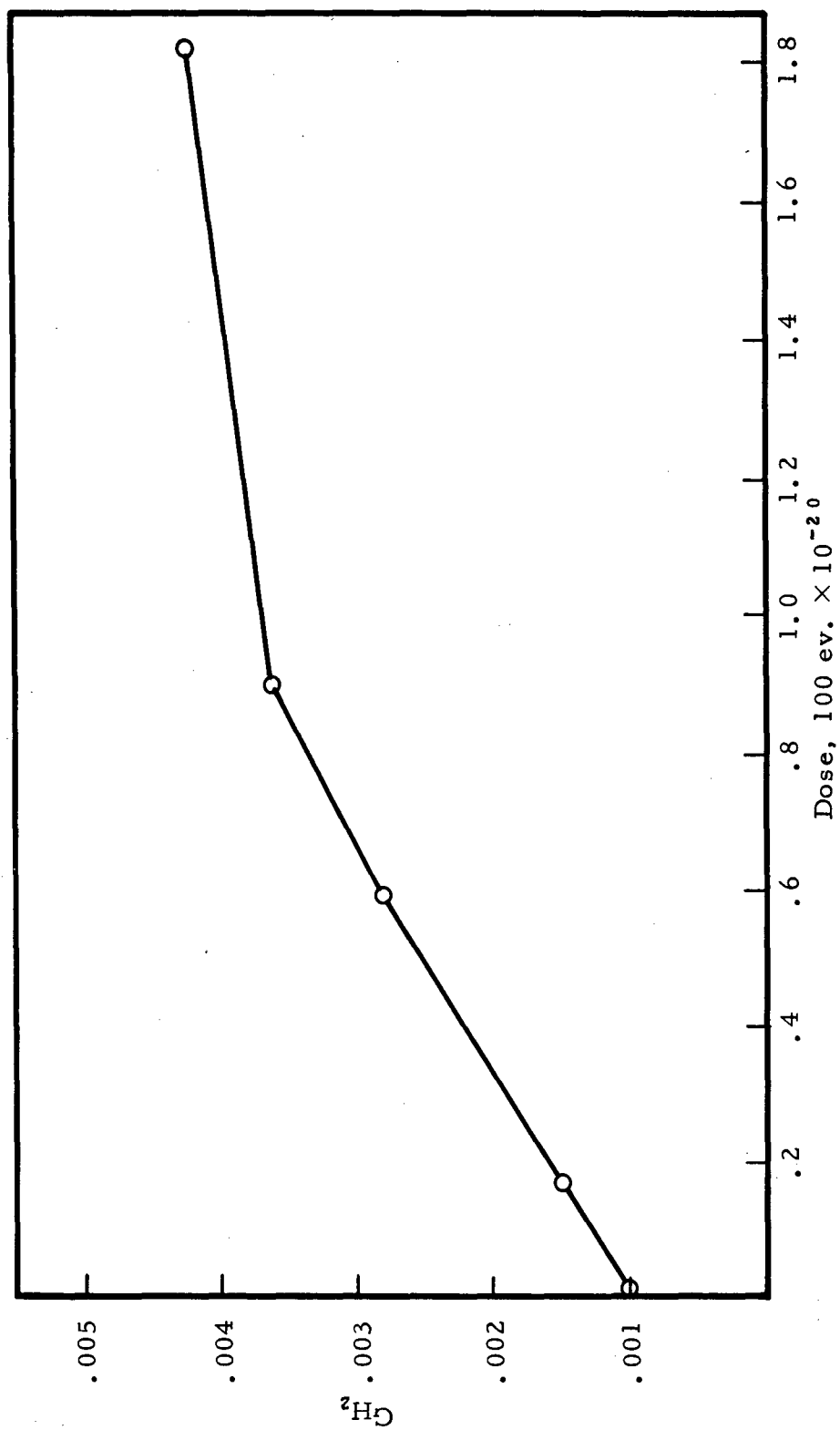
Figure 14. The Yield of Hydrogen from the Radiolysis of Diphenyl Ether.

8.   Polymer Formation and Diphenyl Ether Disappearance

The data shown in Table 8 related to polymer formation and the rate of diphenyl ether disappearance are plotted in Figure 15. The determination of the $-G_m$ value was made by gas chromatography. It was impossible to determine, by the methods available, an accurate $-G_m$ value for irradiations in the low- and medium-dose regions. Point A, Figure 15, represents a $-G_m$ value obtained for a minimum high-dose irradiation and this value is thought to have considerable error. The error in determination of point B should be somewhat less than point A, and point C should be a reasonably accurate value. Line D, through points B and C should represent a maximum $-G_m$ value for the irradiations of diphenyl ether. It is altogether possible, though not likely, that the rate of diphenyl ether disappearance is constant throughout the irradiation range and may not be significantly greater than 0.5 at any dose. Line D represents a liberal interpretation of the best available analytical data related to the $-G_m$ values.

The data represented by the G polymer curve, Figure 15, was obtained by combining several of the 2 ml. irradiated diphenyl ether samples and allowing the ether to evaporate at atmospheric pressure while heating at temperatures not exceeding 180°C. This technique permitted the removal of the low-boiling yield products, the diphenyl ether and materials boiling lower than the 4-phenyl ethers. The G polymer was then calculated in terms of the number of molecules of diphenyl ether required to be equivalent to the residue weight. The G polymer curve should represent reasonably accurate values and shows that the rate of polymer formation increases with increasing dose up to the dose region designated previously as the high-dose region. In the high-dose region the rate of polymer formation appears to be almost constant. The number average molecular weight of the polymer represented by point C, Figure 15, was found to be 625.

9.   Determination of Biphenyl in the Radiolysis of Diphenyl Ether

If phenyl radicals are formed in the radiolysis of diphenyl ether, one could expect a certain amount of radical-radical combination reactions which would result in the formation of biphenyl. A biphenyl yield of 0.0011 has been reported by Wagner and Towle.[4] This is a low yield and was obtained from a very high-dose irradiation, 7.05×10^{22} 100 ev. by 1-Mev electrons.
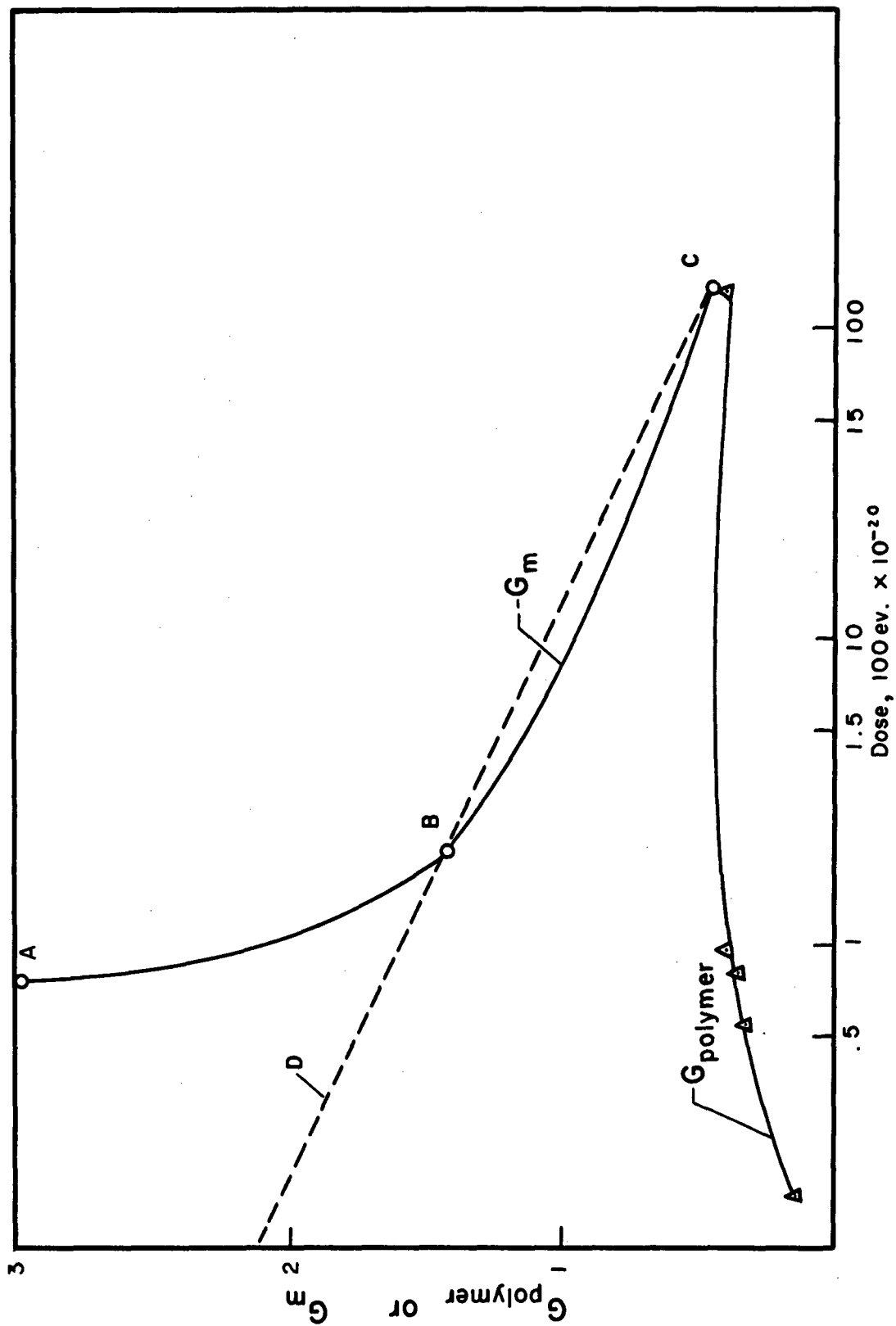
Figure 15. Rate of Diphenyl Ether Disappearance and Polymer Formation as
Related to Energy Absorbed.

Considerable research effort was expended in trying to develop gas chromatographic methods that would separate adequately small amounts of biphenyl from diphenyl ether. These compounds, boiling at 255°C. and 259°C. respectively, are rather difficult to separate. Using a Dow Silicone 710 six foot column operating at 190°C., it was found that a trace amount of biphenyl in the presence of diphenyl ether could be detected only by the shape of the beginning part of the diphenyl ether chromatogram peak; there was no complete resolution of the components. Based on the circumstances of the analysis for biphenyl it is felt that the gamma radiolysis of diphenyl ether does not produce biphenyl in quantities greater than that reported by Wagner and Towle and in all probability, the compound is not formed at all.

V.   DISCUSSION OF EXPERIMENTAL RESULTS

A.   Summary of Experimental Results

This section, through a discussion of experimental results, presents a possible mechanism for the radiolytic degradation of diphenyl ether. As an aid to this discussion, the following paragraphs summarize briefly the pertinent information obtained from the data and observations in Section IV.

(1) High-dose irradiations of large samples of diphenyl ether give yield values as indicated for the following components:

	Product	G Value (Sec. IV, Par. A)
(a)	hydrogen	.004
(b)	carbon monoxide	.0006
(c)	benzene	.036
(d)	phenol	.200
(e)	o-diphenoxybenzene	.0403
(f)	m-diphenoxybenzene	.0165
(g)	p-diphenoxybenzene	-----
(h)	4-biphenylyl phenyl ether	.0082
(i)	bis(m-phenoxyphenyl) ether	-----
(j)	bis(p-phenoxyphenyl) ether	-----
(k)	o-phenoxyphenol	.0215
(l)	p-phenoxyphenol	.0124
(m)	p-phenylphenol	-----

(2) Yield components detectable by gas chromatography account for about 10% of the degraded ether (Sec. IV, Par. A).

(3) Radiation greatly increases the viscosity of the ether indicating considerable polymer formation (Sec. IV, Par. A).

(4) Spectroscopic examination of fractions and irradiated ethers show the presence of small amounts of aliphatic or saturated cyclic and carbonyl structures and considerable 1:3 and 1:4 aromatic substitution (Sec. IV, Par. A).

(5) Sublimation and molecular weight determination of the polymer indicates a rather high degree of polymerization (Sec. IV, Par. A).

(6) Weakly acidic materials other than phenol are formed in quantities about equivalent to the phenol formation (Sec. IV, Par. A).

(7) Dilatometry shows that the diphenyl ether radiolysis proceeds first by scission reactions predominating at low doses followed by an increase in the rate of polymerization reactions as the dose is increased (Sec. IV, Par. B).

(8) The rate of phenol formation is increased as the sample diameter (radiation track length) is increased indicating that the initial processes responsible for phenol formation must occur in or very near the radiation track (Sec. IV, Par. B2).

(9) High dose rate irradiations produce phenol and other phenolic materials. At low dose rates the formation of phenolic materials other than phenol is reduced and is not detectable (Sec. IV, Par. C2).

(10) The rate of phenol formation is nearly independent of the temperature of irradiation indicating that the process responsible for phenol formation is not dependent upon radical diffusion but occurs in or near the radiation track. The rate of formation of phenolic materials other than phenol is dependent, however, upon the temperature of irradiation and is thus indicated to be a function of radical diffusion (Sec. IV, Par. C3).

(11) The irradiation of standard 2 ml. samples of diphenyl ether gives a $G_{benzene}$ ranging from 0.0368 to 0.0488 and a G_{phenol} ranging from 0.2169 to 0.2795. The ratio of phenol yield to benzene yield varies from 5.4 to 6.4 (Sec. IV, Table 8).

(12) In proper concentrations DPPH is an ideal radical scavenger. This scavenger gives a G free-radical value of 0.94 (Sec. IV, Par. D1).

(13) The rate of detectable radical formation increases as the temperature of irradiation is increased and is probably a function of radical diffusion (Sec. IV, Par. D1).

(14) The rate of radical formation is not effected by dose rate (Sec. IV, Par. D1).

(15) Phenol added to diphenyl ether prior to irradiation does not affect the rate of phenol formation. The yield of benzene is increased slightly by the addition of phenol (Sec. IV, Par. D2).

(16) Polyaryl ethers and phenols present as additives do not affect the phenol and benzene yields. The polyaryl phenols reduce to a small degree the yield of total phenolic material (Sec. IV, Par. D2).

(17) Diphenyl ether, polyaryl ethers, and polyaryl phenols possess rather efficient "energy transfer" characteristics as far as reducing the hydrogen yield from cyclohexane is concerned (Sec. IV, Par. D3).

(18) Phenyl radicals formed in situ react with diphenyl ether to form many compounds found in the radiolysis of diphenyl ether. Of major significance is the formation of phenol from the action of phenyl radicals with diphenyl ether. No hydrogen is formed by the reaction. An increased concentration of phenyl radicals (from benzoyl peroxide) in the ether during an irradiation results in an increase in phenol formation with an insignificant increase in benzene (Sec. IV, Par. D4).

(19) Phenyl radicals formed in situ react with other compounds structurally similar to diphenyl ether to form compounds analogous to phenol, i. e. toluene is formed from diphenyl methane, aniline from diphenyl amine, and m-cresol from bis(3-methylphenyl) ether (Sec. IV, Par. D5).

(20) Phenoxy radicals formed in situ appear to be responsible for the formation of high-boiling compounds in which phenyl groups are separated by oxygen linkages (Sec. IV, Par. D6).

(21) The rate of diphenyl ether disappearance decreases with increasing radiation dose and may become constant at high doses, $-G_m = 0.4-0.5$ (Sec. IV, Par. D8).
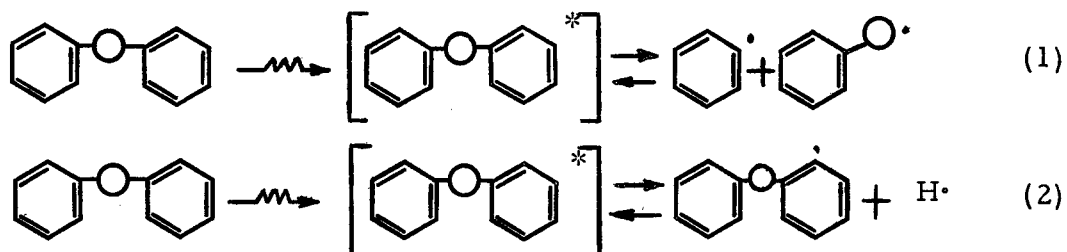
(22) The rate of polymer formation increases and then becomes constant in the high dose region and approaches the rate of diphenyl ether disappearance.

(23) No evidence for the formation of biphenyl from the radiolysis of diphenyl ether was found (Sec. IV, Par. D9).

B.   Theoretical Considerations of Probable Reactions Occurring in Diphenyl Ether Radiolysis

The diphenyl ether molecule contains C-C, C-H, and C-O bonds. Of these, the bond energy of the C-O is the smallest (Table 2) and consequently should be the most susceptible to cleavage during radiolytic degradation. The energy of the radiation used in this investigation would be sufficient to break all the bonds except where energy transfer mechanisms are effective in minimizing the bond

scission. Radiolysis studies of the aromatic hydrocarbons show that
very little rupture of the aromatic ring occurs and consequently direct
radiolytic cleavage of the C-C bonds in the ether molecule would not
be expected. The C-H bond cleavage in the radiolysis of aromatic
hydrocarbons occurs only to a minor extent. Therefore, radiolytic
cleavage reactions in diphenyl ether would involve predominantly the
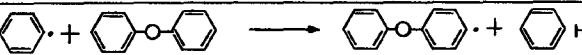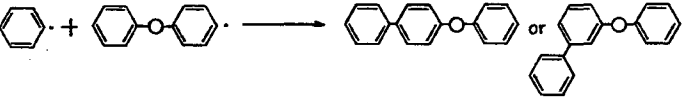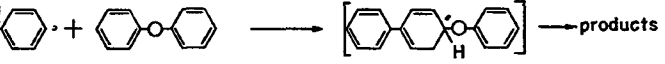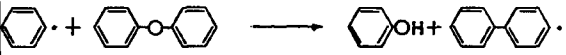C-O bonds as indicated in the following two primary radiolysis equations:

$$\phi\text{-O-}\phi \xrightarrow{\sim\sim} [\phi\text{-O-}\phi]^* \rightleftarrows \phi\cdot + \phi\text{-O}\cdot \qquad (1)$$

$$\phi\text{-O-}\phi \xrightarrow{\sim\sim} [\phi\text{-O-}\phi]^* \rightleftarrows \phi\text{-O-}\dot\phi + \text{H}\cdot \qquad (2)$$
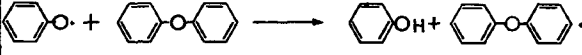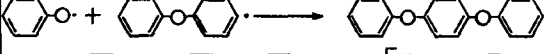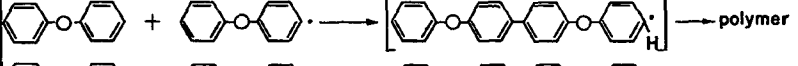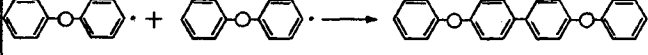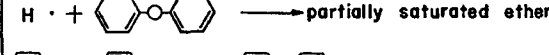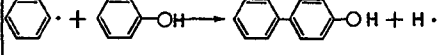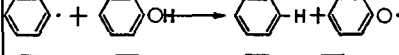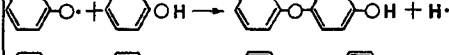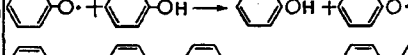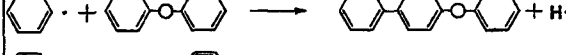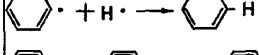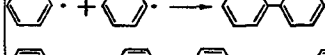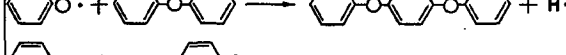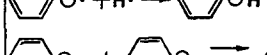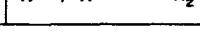
The formation of free radicals by either of the above reactions
is considered to be the primary reaction. The chemical changes observed
as the result of radiolysis are subsequently induced by the reaction of
these free radicals. The reaction of these free radicals with other
radicals or molecules producing the observed changes are considered to
be secondary reactions and the most probable of these occurring in the
radiolysis of diphenyl ether are presented in Table 10.

Reactions 13, 16, and 19 are unlikely to predominate because they
are probably endothermic (see reaction 1, Sec. II). Reaction 18 can be
eliminated from consideration since the radiation environment would
cause immediate cleavage of the weak peroxide bond. Reactions 14, 15,
and 17 are thermodynamically possible; however, the probability of
these reactions occurring to a measurable degree is rather low since
the reactivity of the phenyl radical is quite high and this radical should
be consumed rapidly by other processes before reactions 14 and 15 could
occur. The reactivity of the H· and the susceptibility of the aromatic
molecules for reaction with the hydrogen atom or phenyl radical makes
reaction 17 very improbable. The energetics for reactions 11 and 12
might be favorable; however, the probability for the occurrence of
these reactions would be dependent upon the formation of phenol and
this probability would be quite low at low absorbed doses. Reaction
11a, phenolic hydrogen atom abstraction by the phenyl radical, would
be thermodynamically preferred; however, the reaction probability
would be quite low. Reaction 12a could proceed through a resonant
process and would be a preferred reaction if the reactive species were
present in sufficient concentrations. Reaction 8 is energetically feasi-
ble, probable and preferred if the diphenyl ether radical is formed.
Reaction 9 is very probable particularly if activated ether molecules

TABLE 10

PROBABLE SECONDARY FREE RADICAL RE-ACTIONS OCCURRING IN THE RADIOLYSIS OF DIPHENYL ETHER

No.	Reaction Equation
3	(structural reaction)
4	(structural reaction) ... or ...
4a	(structural reaction) → products
5	(structural reaction)
6	(structural reaction)
7	(structural reaction)
8	(structural reaction) → polymer
9	(structural reaction)
10	H· + (structural) → partially saturated ether
11	(structural reaction)
11a	(structural reaction)
12	(structural reaction)
12a	(structural reaction)
13	(structural reaction) + H·
14	(structural reaction)
15	(structural reaction)
16	(structural reaction) + H·
17	(structural reaction)
18	(structural reaction)
19	(structural reaction)
20	$H \cdot + H \cdot \longrightarrow H_2$

can be degraded to radicals without bond scission. Hydrogen formation via reaction 20 is very unlikely to occur since the reactivity of the hydrogen atom is great enough to assure its consumption by other methods, such as reaction 10, before reaction 20 could occur.

Although little can be said regarding the thermodynamics of the secondary reactions 3-12, they may be used conveniently to account for many of the products found in radiolytically decomposed diphenyl ether. Based on probability considerations these reactions are more likely to occur than many of the other reactions. Further statements regarding reactions 1-12 appear in the following section.

C.   Considerations of Radiolytic Mechanisms in Diphenyl Ether Degradation

In the low-dose irradiation region it must be assumed that the primary degradation step is that indicated by reaction 1. This assumption is validated by the dilatometry studies within limitations, since it is known that some polymerization reactions do occur in this dose region.

Free-radical scavenger studies (DPPH) show that the rate of radical formation is 0.94 radicals per 100 ev. of absorbed energy. Thus, using the above argument, the initial yields from reaction 1 are as follows:

-0.47   0.47   +   0.47
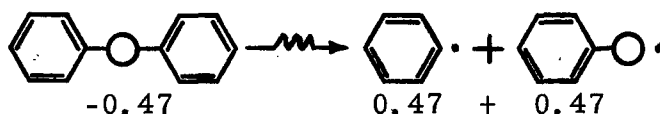
The fate of the phenyl and phenoxy radicals is of primary importance. Since reaction 1 demands that these radicals be formed in equal quantities and since the observed benzene and phenol concentrations are not equivalent, it must be concluded that most of these radicals enter into reactions more complex than simple hydrogen abstraction.

If it is assumed that benzene is formed by a hydrogen abstraction reaction (reaction 3) and the observed $G_{benzene}$ is 0.036, then reaction 3 accounts for the consumption of 7.7% of the phenyl radicals formed by reaction 1.

The G values of the other reactions involving the phenyl radicals must account for a phenyl radical G value of 0.434.

Reaction 4 could occur; however, its probability is rather low as it is dependent upon the formation of an ether radical. Reaction 4a is energetically feasible and has a high probability for occurrence since its environment is always composed of a high concentration of ether molecules. For discussion purposes, reactions 4a and 5 should be considered identical except for the position of attack of the phenyl radical on the ether molecule. In reaction 4a it is proposed that the phenyl radical attacks the ether molecule at the meta and/or para positions, thus forming an active complex which can stabilize itself (a) by losing a hydrogen atom to produce a biphenylyl phenyl ether, or (b) by reacting with other radicals or activated molecules to form higher molecular weight products.

In reaction 5, the phenyl radical attacks the ether molecule in the ortho position, forming an active complex which is immediately degraded into phenol and the biphenylyl radical. If all the remaining phenyl radicals (G = 0.434) were to react via reaction 5 to form phenol, one would expect a G_{phenol} of 0.434 from the radiolysis of the ether. This high yield of phenol was not observed; the yield was about 0.22. In other words, based on the observed phenol yield, reaction 5 consumes about 51% of the available phenyl radicals.

It is proposed that reaction 5 is the predominating phenol-forming reaction and justification for this statement is outlined below:

(1) Table 1 shows that phenyl radical reactions with aromatic compounds result in isomer distributions in which the ortho isomer accounts for 48% to 67% of the products. If 48% to 67% of the available phenyl radicals (G = 0.434) were to react at the ortho position of diphenyl ether to form an active complex which subsequently decomposed to form phenol, one would expect to find a phenol yield of 0.21 to 0.29. This expected yield coincides with the experimentally observed value (0.22).

(2) The fact that the theoretically calculated yield corresponds to an observed yield is not proof of a proposed mechanism; however, it does give considerable support to the proposal. The proposed reaction sequence for the phenol-forming mechanism is depicted in reaction 5a.

$$(5a)$$
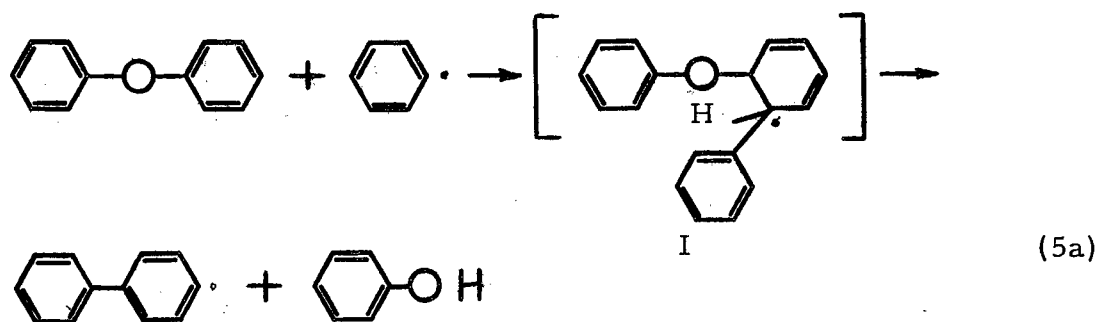
The complex radical I should be highly unstable and would immediately decompose into the products. (Note the similarity of this reaction to reaction 5, Sec. II). The formation of a stable yield product derived from (I) was not indicated by any of the product analysis techniques, i.e. gas chromatography did not show the presence of a component that could be 2-biphenyl phenyl ether nor did spectroscopy studies indicate any significant quantities of 1:2 aromatic substitution.

(3) In order to confirm the above mechanism, one would have to tag or block the four ortho positions in the ether molecule which would be a rather difficult task. Some evidence to support this mechanism was obtained, however, by determining the phenol yield from the isomeric diphenoxybenzenes. If the above mechanism is functional in the formation of phenol from these ethers, then the radiolytic phenol yield from these ethers would be proportional to the number of center ring ortho positions in the molecule. This expectation is at least partially confirmed by the data shown in Table 11.

TABLE 11

PHENOL YIELD FROM THE RADIOLYSIS OF DIPHENOXYBENZENES

Compounds	$G_{(phenol)}$	Center ring ortho positions
o-diphenoxybenzene	0.055	2
m-diphenoxybenzene	0.158	3
p-diphenoxybenzene	0.140	4

The fact that p-diphenoxybenzene does not follow the above expectations is not too disturbing since it is well known that para substituted isomers are much more radiolytically stable than the corresponding ortho and meta isomers.

If phenol is formed via reaction 5a, there is available a G value equivalent to 0.21 to 0.29 of biphenylyl radicals. The experimental data show that very little, if any, biphenyl is formed; therefore, this radical does not react by mechanisms analogous to those of reactions 3 or 14. It is presumed that this radical forms products of higher molecular weight as indicated in reaction 21.

(21)

With the analytical techniques presently available it is difficult to distinquish the product of this reaction from products of other reactions such as 8 and 9. The only evidence to indicate that products of this type are formed is that spectroscopic examination of an irradiated diphenyl ether shows the presence of 1:3 and 1:4 aromatic substitution.

The remaining phenyl radicals (those not reacted by reactions 3 and 5) are presumed to be involved in reactions with the meta and para positions of the diphenyl ether (see reaction 4, Table 10).

The role of the phenoxy radical in the formation of the radiolytic products of diphenyl ether is not as clearly defined as that of the phenyl radical because the phenoxy radical could not be formed independently in situ. The only experimental evidence indicative of the type of compounds formed by the phenoxy radical comes from phenoxy radicals formed in situ in the presence of phenyl radicals formed simultaneously. Phenoxy radicals cause an increase in the formation of high molecular weight compounds in which the phenyl groups are separated by oxygen linkages, i.e. diphenoxybenzenes. This is the type of compound expected from reaction 7 or possibly reaction 16. The diphenoxybenzenes are the first high-boiling compounds detectable by gas chromatography; they become detectable in the medium dose region. For lack of information to indicate otherwise it must be assumed that the entire yield of phenoxy radicals (G = 0.47) is used in forming diphenoxybenzenes.
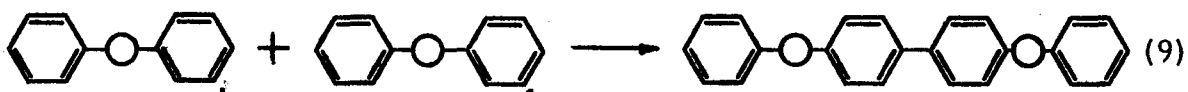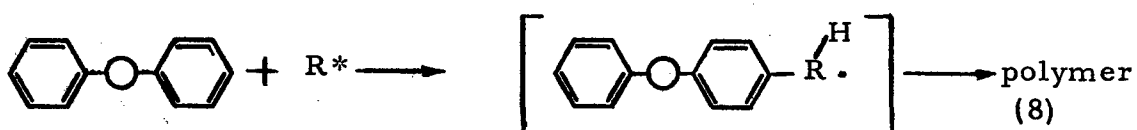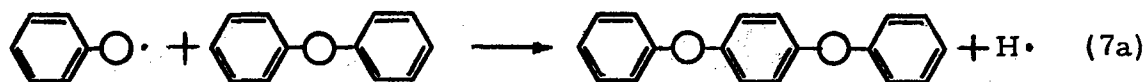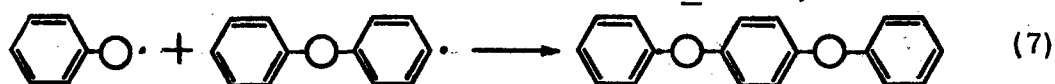
Phenol formation from the phenoxy radical by reaction 6 cannot be ruled out; however, it would not be expected to form phenol at a

rate greater than reaction 3 forms benzene from the phenyl radical.

The rate of polymer formation in low-dose irradiations is quite small but increases as the absorbed dose is increased and approaches a constant G value of 0.4 to 0.5. The exact mode of polymer formation is not known. Experimental data show that polymerization must proceed via a reaction whereby rather high-molecular-weight materials are formed. This is indicated by the rapid increase in density and viscosity of the ether irradiated to high doses and by the fact that a polymer fraction was shown to have a molecular weight of 17,000. Also, the number average molecular weight of the total polymer (all yield components boiling higher than the diphenoxybenzenes) was found to be 625, which is indicative of the presence of very high-molecular-weight polymer molecules. A reasonable process by which such polymers could be formed would be by a radical initiated chain reaction as indicated by reaction 8. At present there is no way to identify the radical species responsible for initiating the reactions; however, it is quite likely that they are formed from a primary reaction such as reaction 2 or arise from secondary reactions such as 3, 5 or 6. The fact that the polymer-formation rate is quite low at low doses indicates that this reaction is dependent upon the concentration of the initiating radicals. If primary reaction 2 does occur, it should form radicals at a constant rate throughout all irradiation-dose regions and, consequently, if the polymerization is dependent upon these radicals, the rate of polymer formation should be constant, even at low doses. It is, therefore, probable that the initiating radicals are derived from the secondary reactions and the primary reaction 2 may not occur at all. Many of the radicals formed from the secondary reactions such as 3 and 6 may enter into radical-combination reactions like reaction 9. Products of this type could be classed as low-molecular-weight polymers. High-temperature gas chromatography shows the presence of compounds of this type in an irradiated ether. These were previously identified (Sec. IV, Par. A) by HTC as being bis(phenoxyphenyl) ethers. The bis(phenoxy)biphenyl depicted as resulting from reaction 9 could very well be indistinquishable by gas chromatography from the bis(phenoxyphenyl) ethers.

D.   Summary of the Most Probable Degradation Mechanisms

The following reactions seem to be the most probable ones responsible for the degradation of diphenyl ether. These reactions can account for most of the observed radiolytic products and yield values.

(1)

(3)

(4)

$\underline{m}$ or $\underline{p}$ -   → products
(4a)

$\underline{o}$-, only   (5 or 5a)

(7)

+ H•   (7a)

+ R* →   → polymer
(8)

(9)
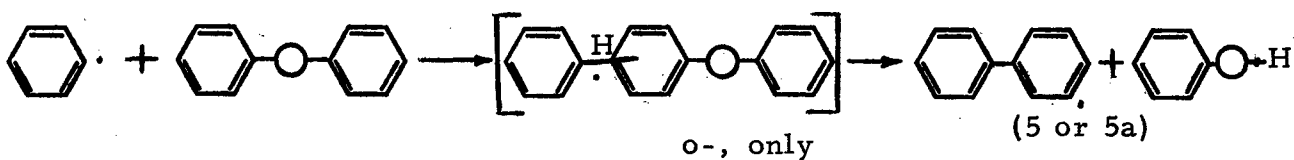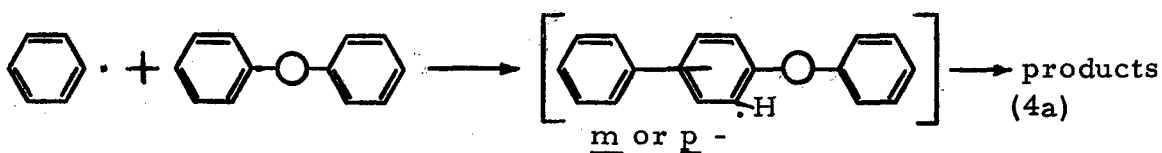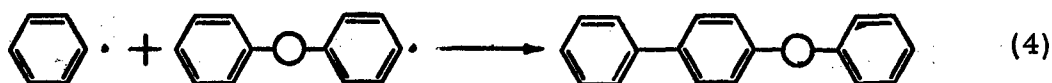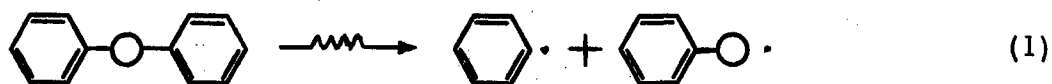
*R = any radical produced by secondary reactions.

Other reactions of minor significance are known to occur and these will be discussed later.

E. Material Balance

The following is an attempt to derive a material balance for the radiolysis of diphenyl ether at low doses in terms of yield values determined experimentally or calculated from assumptions made in proposing radiolysis mechanisms.

Reaction 1

$[-0.47*]$ $- G_{DPPH} = .94$ $\underline{0.47}$ 0.47

Reaction 3

$.036$ $.036*$ $\underline{.036} + .036$

Reaction 4a

  products

$[.21]$ $.21*$ $.21$

Reaction 5

$.22$ $.22*$ $\underline{.22}$ $.22$

Reaction 7

$[.47]$ $.47*$ $.47$

Reaction 8

  polymer

$<.2*$ $\underline{<.2}$
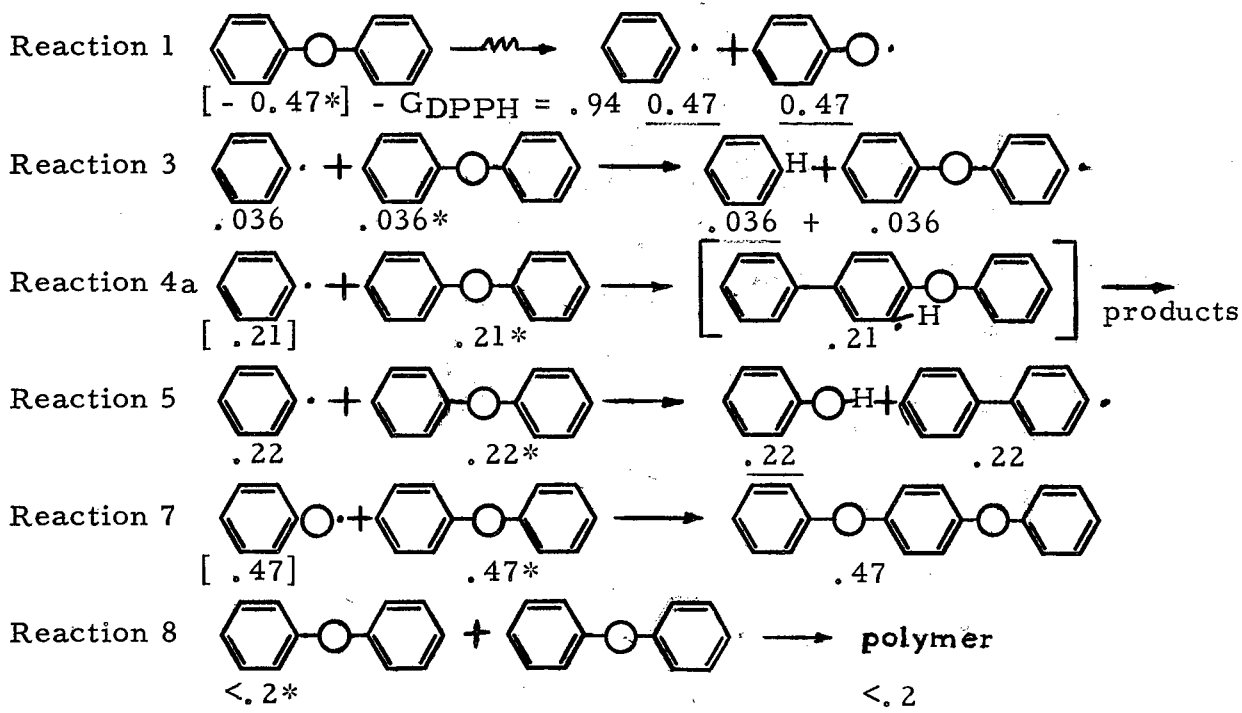
The underlined yield values are experimentally determined; the bracketed values are calculated or assumed from the proposed mechanism; and the remaining are indicated only to show a reaction balance. Summation of the above values which are directly related to consuming diphenyl ether (value marked with *) gives a theoretical $-G_m$ value for diphenyl ether of 1.61, which corresponds to a maximum experimentally estimated $-G_m$ value of 2.1 for a very small dose, (see Figure 15).

F. Kinetic Considerations

The scission of the ether bond with the formation of phenyl and phenoxy radicals has been shown to be the predominant reaction in the radiolysis of diphenyl ether at low doses. At these dose levels the concentration of the ether remains for all practical purposes constant and its decomposition rate should, therefore, follow a zero-order kinetic expression. Since it is difficult to follow analytically the small concentration changes of the diphenyl ether, the rate of radical formation

was measured and was used to indicate the rate of diphenyl ether disappearance. Using DPPH as radical scavenger and assuming only the formation of phenyl and phenoxy radicals, the following equations indicate the relation of ether disappearance to scavenger disappearance.

$$\phi\text{-}o\text{-}\phi \rightarrow \phi\cdot + \phi o\cdot \tag{1}$$

$$\phi\cdot + \phi o\cdot + 2\,DPPH \rightarrow \phi\,DPPH + \phi o\,DPPH \tag{2}$$
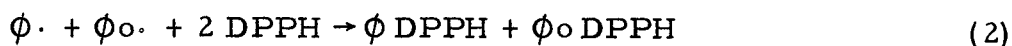
The overall reaction can thus be represented as follows:

$$\phi\text{-}o\text{-}\phi + 2\,DPPH \rightarrow 2\,R*DPPH \tag{3}$$

$$*R = \phi\cdot \text{ and } \phi o\cdot$$
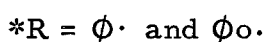
Since the disappearance of one molecule of diphenyl ether corresponds to that of two molecules of scavenger and the appearance of two molecules of reaction products, it follows that the rate of reactions are related by the expressions:

$$-\frac{d[DPPH]}{dt} = -2\,\frac{d[\phi\text{-}o\text{-}\phi]}{dt} = \frac{d[R\,DPPH]}{dt} \tag{4}$$

therefore:

$$-\frac{d[\phi\text{-}o\text{-}\phi]}{dt} = -\frac{1}{2}\,\frac{d[DPPH]}{dt} \tag{5}$$

Since the absorbed dose D is a direct function of time, it follows that dt is a direct measure of absorbed dose dD; therefore, equation (5) can be written as follows:

$$-\frac{d[\phi\text{-}o\phi]}{dD} = -\frac{1}{2}\,\frac{d[DPPH]}{dD} \tag{6}$$

The rate of disappearance of the ether is half the rate of disappearance of the scavenger molecules.

If the absorbed dose is expressed in 100 ev. units (D = 100 ev.), then the rate of disappearance is equivalent to the radiolytic yield value (G). Therefore, the G value for the disappearance of the diphenyl ether molecule ($-G_m$) can be expressed as a function of the rate of the disappearance of the DPPH molecules:

$$- \frac{d[\phi\text{-o-}\phi]}{dD} = -G_m = \frac{1}{2} \frac{d[DPPH]}{dD} \qquad (7)$$

where [DPPH] and [ϕ-o-ϕ] is expressed as number of molecules.

The disappearance of DPPH at low doses was determined experimentally and is represented in curve 5, Figure 10 (Sec. IV, Par. D1). The linearity of curve 5 indicates that the rate of disappearance of DPPH follows a zero-order expression. From this curve it can be calculated that the rate of DPPH disappearance is 0.94 molecules per 100 ev. Therefore,

$$- \frac{d[DPPH]}{dD} = 0.94 \text{ then} - \frac{1}{2} \frac{[DPPH]}{dD} = -G_m = 0.47 \qquad (8)$$

From equations 7 and 8 it follows that:

$$- \frac{d[\phi\text{-o-}\phi]}{dD} = -G_m = 0.47 \qquad (9)$$

and this value represents the disappearance rate of diphenyl ether resulting from scission of the ether bond.

Expressed in other units, the rate constants for $-G_m$, G_ϕ. and $G_{\phi o}$. would all have the value of 0.504×10^{-6} molecules/liter-hour when the radiation dose rate is about 5×10^{-5} r./hr. for a standard two milliliter sample being radiated at 26°C.

If most of the radicals produced by scission are reacting directly with the diphenyl ether, as previously indicated, one would expect that the rate of diphenyl ether disappearance should be of zero-order. This rate of disappearance should be three-fold greater than the rate of phenyl radical or phenoxy radical formation. Figure 16 shows the relation of diphenyl ether disappearance to radiation dose. The linearity of the curve between points A and B indicates that the disappearance of the ether follows zero-order kinetics. The slope of this curve is equal to the $-G_m$ and is 1.77. This compares to an expected value of 1.41 which is based on the assumption that the total $-G_m$ should equal three times the yield of phenyl or phenoxy radicals. At doses greater than 10^{20} (100 ev.) the linearity of this curve ceases and it is presumed that other reactions are affecting the rate of diphenyl ether disappearance. The rate of diphenyl ether disappearance
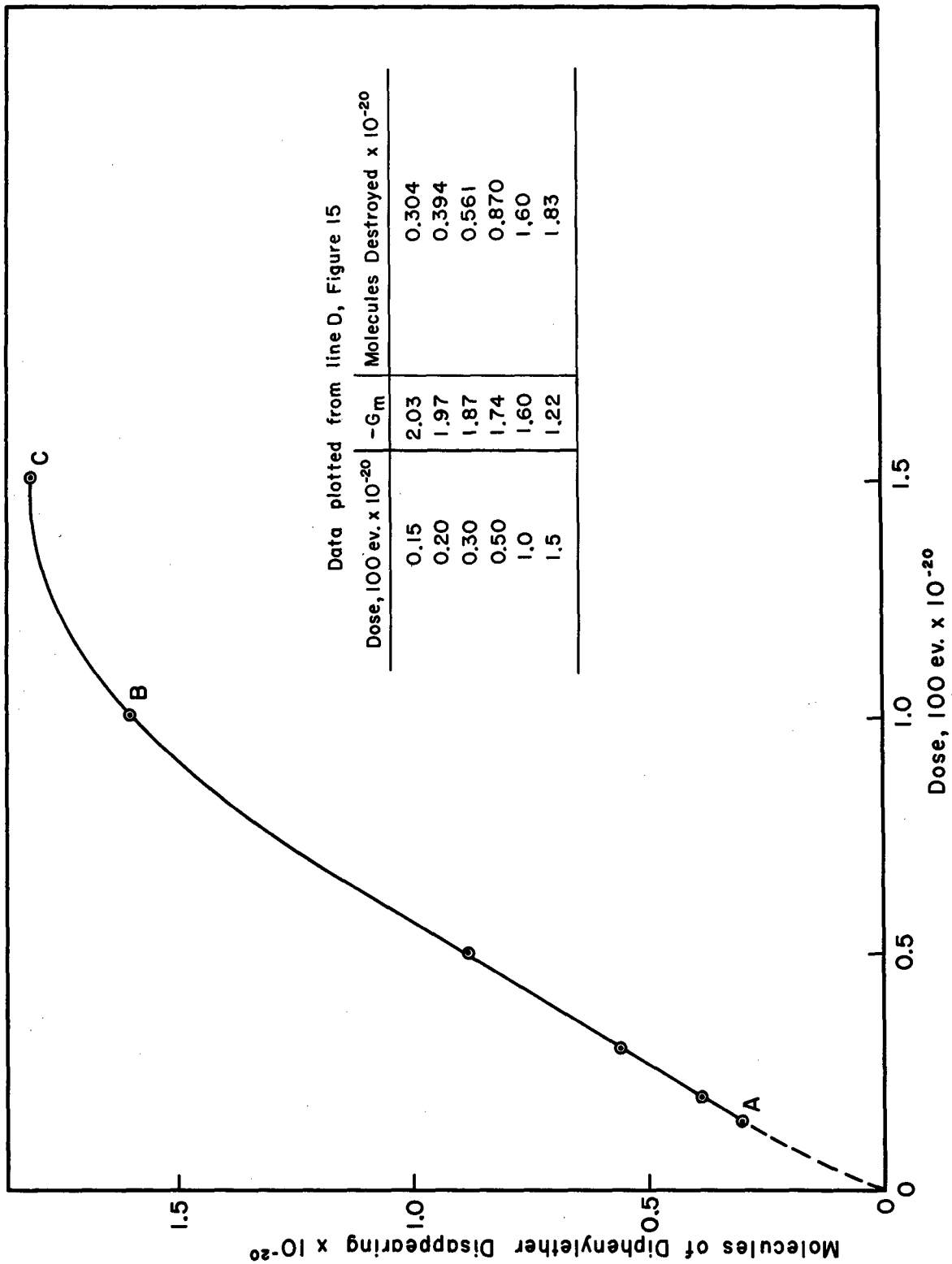
Figure 16. Relation of Diphenyl Ether Disappearance ($-G_m$) to Radiation Dose.

Data plotted from line D, Figure 15

Dose, 100 ev. x 10^{-20}	$-G_m$	Molecules Destroyed x 10^{-20}
0.15	2.03	0.304
0.20	1.97	0.394
0.30	1.87	0.561
0.50	1.74	0.870
1.0	1.60	1.60
1.5	1.22	1.83

is decreased considerably at doses greater than 10^{20} (100 ev.). It should be noted that the dose indicated by point B, Figure 16, corresponds very closely to point C, Figure 5. The interpretation of the latter is that at these absorbed doses, a polymerization reaction is predominating over the ether bond scission (see Sec. IV, Par. 1B). It is very probable that the reactions responsible for the change in rate of ether disappearance indicated by the curve between points B and C, Figure 16, is the result of this polymerization reaction.

G.   Minor Radiolytic Reactions

The formation of hydrogen in the radiolysis of diphenyl ether is quite low. Though not actually observed, hydrogen is believed to be formed at a rather constant rate over the entire radiation dose range (see Sec. IV, Par. 7). Considerable work has been reported concerning the mode of hydrogen formations in the radiolysis of aromatic hydrocarbons[52, 53] and much evidence indicates that hydrogen atoms arising from a dissociation such as reaction

$$\text{RH} \xrightarrow{\hspace{1cm}} \text{RH*} \xrightarrow{\hspace{1cm}} \text{R} \cdot + \text{H} \cdot \qquad (1)$$

are consumed by addition to the surrounding aromatic hydrocarbon.

Since the observed hydrogen yield from the radiolysis of diphenyl ether is similar to that found from the radiolysis of analogous hydrocarbons, i.e. biphenyl and terphenyls[54] it is presumed that the presence of the C-O bond in the ether has little or no effect on the mode of hydrogen formation. Hydrogen atoms arising from a reaction similar to (1) above and subsequently reacting with the ether molecules could account for the formation of some of the hydrogenated structures observed by the spectroscopic examination of the irradiated ether or chromatographically separated ether fractions (Sec. IV, Par. A and Table 7). The formation of hydrogen molecules may very well arise from a molecular process involving excited ether molecules from which the reaction products are hydrogen and polymer as shown in reaction 2.

$$\qquad (2)$$
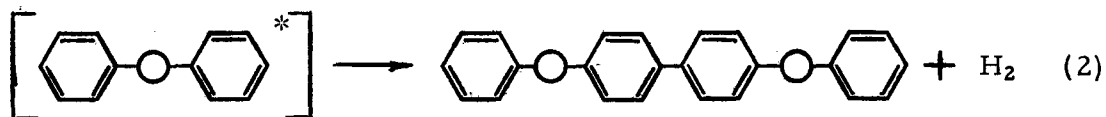
At high doses of radiation there is observed a small yield of carbon monoxide from the diphenyl ether radiolysis. The origin of this product is a matter of speculation. Some attempts have been made to relate the reactions occurring from radiolysis to those occurring from the action of low-energy electrons from the mass spectrograph.[55] Recent studies by Beynon, Lester and Williams[56] propose a mechanism by which CO is removed from the diphenyl ether molecule by the mass-spectrometer electrons to form a stable alkyl-aromatic ion which is one of the predominating peaks in the mass spectra of diphenyl ether. It is reasonable to suppose that a very similar mechanism could result from gamma radiation and could be responsible for the formation of the aliphatic structures that have been observed in the chromatographed fractions of the irradiated ether (Sec. IV, Par. A). The stable ion formed in the mass spectrometer, as proposed by Beynon et al. has structure (I). The one-electron bond in the dotted region can be stabilized by various resonance forms. The aliphatic-aromatic materials found in the irradiated ether could be formed through an intermediate similar to (I).
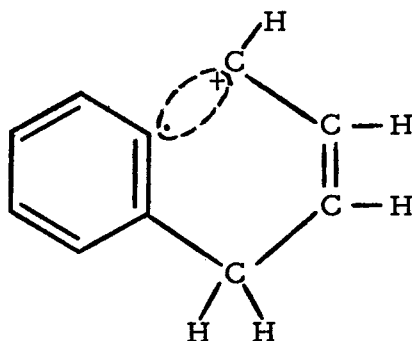
(I)

VI.   CONCLUSIONS

The following general conclusions can be made regarding the radiolytic degradation of diphenyl ether:

1.   Diphenyl ether is quite stable to the effects of gamma radiation. Radiolysis causes the formation of small amounts of hydrogen, carbon monoxide and saturated products; larger quantities of benzene, phenol, higher-molecular-weight phenolic materials, low-molecular-weight polymers and high-molecular-weight polymers.

2.   Physically, radiolysis changes the ether from colorless to dark brown, increases the density and refractive index and greatly increases the viscosity.

3.   The formation of the yield products can be explained by the reactions of free radicals formed by the radiolytic scission of the ether carbon-oxygen bond.   The initial radicals formed by radiolysis of the ether are the phenyl and phenoxy radicals.

4.   The radiolytic scission of the C-O bond would form equivalent quantities of the phenyl and phenoxy radicals.   Most of these radicals do not react by hydrogen abstraction to form benzene and phenol, which are the first-observed yield products.   This is evident because the phenol yield is always five to seven times greater than the benzene yield.

5.   Most of the phenoxy radicals appear to react with the diphenyl ether to form low-molecular weight polymeric materials such as diphenoxybenzenes. A small amount of these radicals may be consumed in forming phenolic materials such as phenoxyphenols.

6.   Phenyl radicals formed in situ in the absence of radiation, in diphenyl ether, can cause the formation of some benzene and major quantities of phenol and other products such as biphenylyl phenyl ethers.

7.   In the absence of radiation, phenyl radicals react with other compounds structurally similar to diphenyl ether to form products analogous to phenol.

8.   Phenyl radicals reacting with aromatic molecules generally substitute predominantly (48-67%) in the ortho position. In diphenyl ether, it appears that about 50% of the radiolytically formed phenyl radicals react at the ortho position of the ether to form a complex which is immediately decomposed to form phenol and another radical.

9.   Phenyl radicals reacting with the ether molecule at the meta and para position do not result in the formation of phenol but form biphenylyl phenyl ether type products.

10.   Evidence to indicate further that phenol formation occurs as the result of phenyl radical reaction with the ortho position of diphenyl ether was obtained from the radiolysis of the isomeric diphenoxybenzenes. The phenol yield from the o-diphenoxybenzene, which has two unsubstituted center ring ortho positions, was considerably less than the phenol yield from the m and p-diphenoxybenzenes, which have, respectively, three and four unsubstituted center ring ortho positions. This indicates that phenol formation is a function of the probability for an ortho position reaction.

11.   The formation of phenyl and phenoxy radicals in the primary degradation process follows zero-order kinetic reactions.

12.   Radiation dose rate (within the limits studied) does not affect the rate of radical formation.

13.   Increasing the temperature of irradiation increases the rate of free-radical formation; this may be a function of radical diffusion processes.

14.   Small quantities of aryl ethers and aryl phenols in cyclohexane are more efficient than benzene in reducing the radiolytic hydrogen yield expected from the cyclohexane. This indicates that these materials are very efficient absorbers of transferred energy and that similar materials formed in the radiolysis of diphenyl ether may be effective in decreasing the rate of the ether degradation as the radiation dose is increased.

15.   Polymer formation appears to be initiated by radicals formed by processes other than the initial formation of phenyl and phenoxy radicals.

Based on all the experimental data, the proposed mechanism for phenol formation is most significant. This proposed mechanism suggests

that phenol is formed from the radiolytically produced phenyl radical reacting at the ortho position of the diphenyl ether molecule to form an unstable complex which is decomposed immediately to form phenol and another radical. The mechanism, though not proved beyond doubt, does appear to be very plausible since it accounts for the high observed radiolytic yield of phenol and the low benzene yield. It also accounts for the formation of the isomeric diphenoxybenzenes, the 3- and 4-biphenylyl phenyl ethers and also the absence of 2-biphenylyl phenyl ether.

RADIOLYSIS OF ARYL ETHERS OF HIGHER MOLECULAR
WEIGHT THAN DIPHENYL ETHER

I.   DISCUSSION OF EXPERIMENTAL RESULTS

It would be very desirable to study the radiolytic mechanisms involved in the radiolysis of the higher-molecular-weight ethers as was done with diphenyl ether. There are several characteristic factors of these ethers which make such a study a difficult task:

(a) The diphenoxybenzenes are solids at temperatures below about 50°C. thus making it necessary to use elevated temperatures for liquid phase irradiations.

(b) At the elevated temperature required for liquid phase irradiations, DPPH could not be used as a radical scavenger since it would be thermally degraded; also, the solubility of DPPH in these ethers is quite limited.

(c) In general, the higher molecular weight ethers are radiolytically more stable than diphenyl ether, thus making the detection of yield products more difficult at low doses of radiation.

(d) Since these ethers are solids or very viscous liquids with high boiling points it is quite difficult to utilize gas chromatography to detect and to determine quantitatively many of the expected yield products.

It can be seen in Table 12 that radiation causes rather large increases in the viscosity of bis[m-(m-phenoxyphenoxy)phenyl] ether m-bis-(m-phenoxyphenoxy)benzene. In this discussion these ethers are referred to as m-6 ether and m-5 ether respectively. This increase, in percent change, is of the same order as that observed from the diphenyl ether radiolysis. Radiolysis of the m-6 ether at 100°C. results in a much larger increase in viscosity change which would indicate that the polymerization reaction responsible for the viscosity increase is temperature dependent. The hydrogen yield from these ethers is of the same order as that observed for diphenyl ether and this could indicate that the hydrogen formation from the radiolysis of ethers is associated with polymer formation.

The yield of benzene and phenol from the radiolysis of the m-5 ether and the m-6 ether is much less than the yield of these products from diphenyl ether. This suggests that in the high-molecular-weight ethers, the rate of C-O bond scission is quite low compared to the scission rate in diphenyl ether.

TABLE 12

ANALYTICAL DATA OBTAINED FROM THE RADIOLYSIS OF SOME HIGH MOLECULAR WEIGHT ETHERS

Compound Irradiated	Bis[m-(m-phenoxyphenoxy)phenyl] ether				m-Bis(m-phenoxyphenoxy)benzene			Monsanto OS 124[a]	
Dose 100 ev. $\times 10^{-22}$	0.653	0.859	0.008	0.021	0.743	0.008	0.021	0.008	0.021
Temp. of Irrad., °C.	100	26	26	26	26	26	26	26	26
n_D^{20} BEFORE	1.6393	1.6393	1.6359	1.6359	1.6283	1.6300	1.6300	1.6301	1.6301
AFTER	1.6405	1.6402	1.6359	1.6361	1.6299	1.6300	1.6300	1.6306	1.6306
Viscosity Chg. (%)									
100°F.	80.3	46.4	---	---	34.5	---	---	---	---
210°F.	21.9	14.1	---	---	17.3	---	---	---	---
Component Yield									
G_{gas}	0.0048	0.0018	---	0.0010	0.006	.0028	0.0020	0.0035	0.0040
G_{H_2}	0.0048	0.0018	---	0.0010	0.006	.0028	0.0020	0.0035	0.0040
$G_{benzene}$	0.0043	0.0021	0.0068	0.0038	0.006	0.0054	0.0031	0.0068	0.0053
G_{phenol}	0.033	0.018	0.073	0.035	0.054	0.077	0.068	0.111	0.0760
$G_{diphenyl\ ether}$	0.002	0.0026	---	trace	0.0018	---	trace	---	0.0010

[a] Monsanto produced isomeric five phenyl ethers.

Other than hydrogen, benzene and phenol, the only low-boiling radiolytic product detectable by gas chromatography was diphenyl ether. The yield of diphenyl ether was very small and this coupled with the low benzene and phenol yields suggests that the C-O bonds located near the center of the ether molecule are not involved in any scission reactions. It is very probable that the energy received by the center part of the large ether molecule is dissipated by energy transfer within the molecule before scission of the internal C-O bonds occurs.

The radiolysis data for Monsanto OS 124 shows that this pilot-plant-produced mixture of isomeric five phenyl ethers (five phenyl groups for each ether molecule) is quite stable to radiation. The yield of benzene and phenol is a little greater than that observed from the radiolysis of the 5-m ether and the 6-m ether but the difference is rather insignificant.

Table 13 shows the analytical data obtained from the radiolysis of m-diphenoxybenzene and 4-biphenylyl phenyl ether. The most obvious difference in the radiolytic stability of these two compounds is the increased stability of the 4-biphenylyl phenyl ether as indicated by the very low benzene and phenol yields. This correlates very well with the data which would be expected if the mechanisms for phenol formation from the radiolysis of diphenyl ether were the same as those responsible for the phenol formation from the 4-biphenylyl phenyl ether. This increased stability may be due partially to the para substitution effects which, in general, makes the para isomer of a series the most radiolytically stable.

The disappearance of m-diphenoxybenzene as the result of radiation appears to be in the same order of magnitude as the disappearance of diphenyl ether. The $-G_m$ values shown in Table 13 can be considered as only reasonable estimates since there was considerable analytical variability in introducing the samples into the gas chromatograph for the analysis.

II.   CONCLUSIONS

1.   Data from radiolysis of bis[m-(m-phenoxyphenoxy)phenyl] ether, m-bis(m-phenoxyphenoxy)benzene and Monsanto OS 124 show that these materials are very stable toward radiolytic degradation as measured by the formation of low-molecular-weight and low-boiling products.

2.   Based on the increase in viscosity resulting from radiation, apparently most of the degradation processes are concerned with the formation of polymeric materials.

3.   The experimental data indicate that C-O bonds located near the center of the large ether molecule are protected from radiolytic scission. This protection may involve energy transfer processes within the ether molecule.

4.   The stability of m-diphenoxybenzene is not significantly greater than that of diphenyl ether. 4-Biphenylyl phenyl ether is very stable toward radiolytic degradation as evidenced by low benzene and phenol yields. This increased stability may be due to a lesser number of free ortho positions which are necessary for phenol formation or may be due to the effects of para substitution which increases the resonance energy of the molecule.

ANALYTICAL METHODS USED IN THE RESEARCH

APPENDIX A

I. ANALYTICAL METHODS USED IN THE RESEARCH

A. Gas Chromatography

1. Gas Yield Determinations

Where irradiation sample size and total dose indicated a sufficient yield of gases for volumetric measurement, the yield gases were transferred from the irradiation cell to a gas burette. The volume was measured at the prevailing pressure and then calculated to STP conditions. Samples of this gas were analyzed with a Beckman GC-2 gas chromatograph (GC-2) using first, for hydrogen determination, a six-foot, 5A molecular sieve column at 40°C. and an argon carrier gas flow rate of 45 ml./min. For components other than hydrogen, such as carbon monoxide, the same column and temperature was used with helium as the carrier gas flowing at 45 ml./min. Gas samples analyzed with a six-foot silica gel column showed that no other gaseous components were present.

Hydrogen yields from the standard 2 ml. low-dose irradiated samples were determined in a different manner. The GC-2, operating at the above conditions for hydrogen determination, was calibrated (a disc integrator was used in each determination to measure peak area) for instrument response to known volumes of hydrogen sampled. Calibration showed the instrument to detect 0.325×10^{18} molecules H_2 per square inch of peak area. The irradiation vial was capped with a short piece of rubber tubing to which was attached a short glass tube sealed with a serum cap. This attached tubing was evacuated through an inserted syringe needle which was then removed and the vial break-off tip opened. A sampling syringe was then used to remove the gases and to make the instrument injection. This step was repeated until the hydrogen peak disappeared from the chromatogram. The sum of the hydrogen peaks was determined and from this and the calibration factor, the total amount of hydrogen produced by the irradiation was calculated.

2. Benzene and Phenol Determination

Several different six-foot columns were investigated in the GC-2 to ascertain the optimum operating conditions. The partitioning materials investigated were asphalt, polyethylene, polyphenyl tar[57], polyester succinate, Apiezon L, DC Silicone 550 and 710, and carbowax 20m. Of

these, the asphalt, 20% on Chromosorb 42/60 mesh, was found to give the most symmetrical peak for small amounts of phenol.

The latter column at 190° or 220°C. with a helium flow rate of 67 ml./min. gave very good resolution between benzene and phenol. Under these conditions the elution time for diphenyl ether was eighteen minutes and this column was, therefore, used for some determinations involving the disappearance of the ether. Instrument calibration for benzene and phenol gave an instrument peak area response of 0.42×10^{18} molecules/in.^{2} respectively. For high dose irradiated samples, 0.02 ml. injections were made to determine the benzene and phenol yield and then the diphenyl ether was allowed to elute from the column. When the determination was to be made from low dose irradiated samples, the GC-2 was equipped with a back-purge attachment. With this attachment, the amount of benzene and phenol in 0.06 ml. samples could be determined and the large amount of ether removed from the column without passing through the detectors.

The back-purge attachment was used to determine the benzene and phenol yields from all ethers boiling higher than diphenyl ether.

After determining the amount of benzene and phenol in a known injected volume, this value was used to calculate the amount of the component present in the total irradiated sample and from this, the yield value was calculated.

3.   Determination of Diphenyl Ether Disappearance ($-G_m$)

Determining the amount of ether destroyed during an irradiation was rather difficult, particularly at low or medium doses, because it involves detecting very small changes in the amount of ether present in a known volume of sample. In order to determine a reasonably accurate value, many separate determinations had to be made on a particular sample.

Most of the $-G_m$ values were calculated from data obtained from analysis using a high temperature gas chromatograph (HTC). This chromatograph was designed after a model reported by Felton[58] and is capable of operating at column temperatures up to 400°C. It was found that a 20% polyethylene column, operating at about 285°C. and a helium flow rate of 65 ml. per min., provided the best method for determining the amount of ether disappearance. At these conditions the diphenyl ether was eluted as a very sharp peak in about

three minutes. The measurement of peak height rather than area was found to be more reproducible as tailing of the ether peak tended to cause a variation in the measured area of the peak.

To make a -G_m determination several (usually 5-10) 0.01 or 0.02 pure ether samples were injected followed by equivalent samples of the irradiated ethers. The average peak height for each was determined and the decrease in peak height of the irradiated ether calculated as a percent of the pure ether peak height. This value was then used to calculate the -G_m.

4.   Determination of Other Components

Yield values of high-boiling components were determined using the HTC operating at column temperatures up to 320°C. and employing the usual gas chromatographic calibration and identification techniques. When available, authentic samples were used for retention time comparison and instrument response calibration.

B.   Spectroscopy

The spectroscopy studies were made using a Baird Infrared recording spectrograph and a Beckman DK 2 visible-ultraviolet spectrograph (DK 2). The usual techniques familiar to spectroscopists were used.

The DK 2 was used to measure the disappearance of the DPPH in the radical scavenger studies. Calibration curves of known concentrations of DPPH in diphenyl ether using the DPPH absorbance band at 5250 Å were utilized to calculate the concentration change of the DPPH resulting from irradiation.

Similar calibration and measurement techniques were utilized to determine total phenolic-OH concentration. Absorbance at 2812 Å was used for the concentration measurement. This method could be utilized for only low and medium dose total phenolic determinations as at higher phenolic concentrations the absorbance-concentration curve did not follow the Beer-Lambert law presumably as the result of solute-solvent association.

C.   Dilatometry

A dilatometer was prepared from a 10 ml. volumetric flask to which was attached a section of thermometer capillary tubing. The assembly was filled with the ether to be irradiated and the temperature

of the dilatometer and solution equilibrated in a water bath at 25.0°C. The liquid level was measured at 25.0°C. on the tubing scale. After a period of irradiation the dilatometer was removed from the source, equilibrated to 25.0°C. and the solution height measured. The liquid level height plotted versus calculated absorbed dose was used to obtain Figure 5 (Sec. IV.)

D.   Micromolecular Weight

A microebulliometer, constructed after the design of Dimbat and Stross[59] was used to determine the reported molecular weights. Under ideal conditions, the instrument can permit the determination of a molecular weight on as little as 10 mg. of sample and can be used to determine molecular weights up to about 20,000. When a sample is a mixture of compounds, indicated molecular weight is a number average molecular weight. The molecular weight calculations were by methods recommended by Bonnar, Dimbat and Stross[60].

RADIATION FACILITIES AND SOURCE CALIBRATION TECHNIQUES

APPENDIX B

II. RADIATION FACILITIES AND SOURCE CALIBRATION TECHNIQUES

The Denver Research Institute Co^{60} source is very similar in design to one used at the University of Notre Dame[61] and is described in detail by Schmidt et al[5]. The source contains approximately 1800 curies of Co^{60}. In the area of maximum intensity the radiation dose rate was about 5×10^5 r./hr. All irradiation dose calculations were corrected for the Co^{60} decay or were determined from direct calibration.

A source calibration was made at different times during the research period using ceric sulfate reduction methods (G = 2.58) as the calibrating dosimeter[62]. The ceric sulfate for the calibrations were contained in sealed pyrex cells of the same type as used for sample irradiations and the concentration was determined spectrophotometrically by measuring the absorbance at 3150 Å.

Late in the research period, the DRI source was cross calibrated with a mobile 2500 curie Co^{60} source operated by Convair under Contract AF 33(616)-7547. The ratio of the intensity of the two sources as measured by the ceric sulfate dosimeter (DRI methods) and the ionization chamber methods used by Convair were within 0.3% of absolute agreement.

COMPOUNDS USED IN THE RESEARCH

APPENDIX C

III.   COMPOUNDS USED IN THE RESEARCH

Table 14 lists the source, purity, and some physical properties of the compounds used in the radiolysis studies. The diphenyl ether used in the radiolysis studies contained no impurities, detectable by gas chromatography, boiling higher or lower than the ether. The other compounds with no detectable impurities contained none boiling lower than the parent compound.

Other compounds used in these studies, primarily for characterization purposes are:

(a) bis(m-phenoxyphenyl)ether

(b) bis(p-phenoxyphenyl)ether

(c) m-phenoxyphenyl p-phenoxyphenyl ether

(d) m-bis[m-phenoxyphenoxy phenoxy] benzene

(e) o-phenoxyphenol

(f) m-phenoxyphenol

(g) p-phenoxyphenol

(h) m-phenoxyphenoxyphenol

(i) p-bis-(p-hydroxyphenoxy)benzene.

The above compounds were supplied as samples by the Monsanto Research Laboratories, Dayton, Ohio.

Diphenylpicrylhydrazyl, used in the radical scavenger studies, was prepared by the method described by Goldschmidt[65] or was obtained from Distillation Products Industries, Eastman Organic Chemicals Department.

TABLE 14

COMPOUNDS USED IN THE RADIOLYSIS STUDIES

	Compound	Source	Purity	mp°C	bp°C
1.	Diphenyl ether	Eastman	NDI	28	259
2.	o-Diphenoxybenzene	Monsanto[a]	>98%	- -	- - - - -
3.	m-Diphenoxybenzene	Eastman	NDI	60	145-51/.3mm[c]
4.	p-Diphenoxybenzene	Monsanto[a]	NDI	75	177/1mm[d]
5.	4-Biphenylyl phenyl ether	Eastman	NDI	68-70	- - - - -
6.	Bis[m-(m-phenoxyphenoxy)phenyl] ether	Monsanto[a]	NDI	oil	335-62/.25mm[c]
7.	m-Bis(m-phenoxyphenoxy)benzene	Monsanto[a]	NDI	oil	295-305/1.0mm[c]
8.	Monsanto OS 124	Monsanto[b]	Mixed isomers	oil	- - - -

a. Monsanto Research Laboratories, Dayton, Ohio
b. Monsanto Chemical Co., St. Louis
NDI = no detectable impurities by gas chromatography
c. Ref. 63
d. Ref. 64

BIBLIOGRAPHY

APPENDIX D

Bibliography

1. Borsoff, V. N., Beaubein, S. J., and Kerlin, W. W., "High Temperature Lubrication in the Presence of Nuclear Radiation," WADD TR 60-424, June 1960.

2. Mahoney, C. L., Kerlin, W. W., Barnum, E. R., Sax, K. J., Saari, W. S., and Williams, P. H., "Engine Oil Development," WADC TR 57-177 Pt. II, February 1958.

3. Kharasch, M. S., Stampa G., and Nudenberg W., Science, 116, 309 (1952).

4. Wagner, M., and Towle, L. H., "Effects of High Energy, High Intensity Electromagnetic Radiation on Organic Liquids," WADC TR-58-206, ASTIA No. 202499, October 1958.

5. Schmidt, J. J. E., Gray, D. N., Bonomo, F. S., and Pomonis, J. G., "Relations Between Structure and Radiation Stability of Various Alkyl Aromatic Fluids," WADC TR 58-377, June 1958.

6. Schmidt, J. J. E., Bohner, G. E., "Relations Between Structure and Radiation Stability of Various Alkyl Aromatic Fluids," WADC TR 58-372 Pt. II, June 1959.

7. Schmidt-Collerus, J. J., and Bohner, G. E., "Determination of the Relations Between Structure and Radiation Stability of Aryl Ether Fluids," WADD TR 60-282 Pt. I, March 1960.

8. Wepfer, G. G., King, L. A., Rice, W. L. R., "Radiation Chemistry and Related Phenomena," WADC TR 59-296.

9. Collinson, E., and Swallow, A. J., Chem. Rev., 56, 471 (1956).

10. Swallow, A. J., "Radiation Chemistry of Organic Compounds," Pergamon Press, New York, N. Y., 1960.

11. Harwood, J. J., Hausner, H. H., Morse, J. G., Rauch, W. G., "The Effects of Radiation on Materials," Reinhold Publishing Corp., New York, N. Y., 1958.

12. Magee, J. L., and Burton, M., J. Am. Chem. Soc., 72, 523 (1950).

13. Burton, M., Magee, J. L., Samuel, A. H., J. Chem. Phys. 20, 760 (1958).

14. Gaumann, T., and Schuler, R. H., *J. Phys. Chem.*, **65**, 703 (1961).

15. Moore, W. J., "Physical Chemistry," Second ed. p. 613-4, Prentice-Hall, Inc., Englewood Cliffs, N. J., 1955.

16. Williams, G. H., "Homolytic Aromatic Substitution," Pergamon Press, New York, 1960, p. 1.

17. Walling, C., "Free Radicals in Solution," John Wiley & Son, Inc., New York 1957, p. 484.

18. Augood, D. R., Hey, D. H., Nechvatel, A., Robinson, T. S., and Williams, G. H., *Research,* **4**, 386 (1951).

19. Augood, D. R., Hey, D. H., and Williams, G. H., *J. Chem. Soc.*, 2094, 1952.

20. Hey, D. H., and Williams, G. H., *J. Chem. Phys.*, **23**, 757 (1955).

21. Augood, D. R., Cadogen, J. I. G., Hey, D. H., and Williams, G. H., *J. Chem. Soc.*, 1953, 3412.

22. Cadogen, J. I. G., Hey, D. H., and Williams, G. H., *J. Chem. Soc.*, 1954, 794.

23. Hey, D. H., Williams, G. H., *Disc. Fara. Soc.*, **14**, 216 (1953).

24. Ref. 17 p. 485.

25. Ref. 17 p. 482-3.

26. Ketelaar, J. A. A., "Chemical Constitution," Elsevier Publishing Co., New York, 1958, p. 205.

27. Benson, S. W., "The Foundations of Chemical Kinetics," McGraw-Hill Book Co., Inc., New York, 1960, p. 670.

28. Steacie, E. W. R., "Atomic and Free Radical Reactions," A.C.S. Monograph No. 125, Reinhold Publishing Corp., New York, 1954.

29. Ref. 28 p. 101-7.

30. Ref. 27 p. 343.

31. Muccini, G. A., and Schuler, R. H., *J. Phys. Chem.*, **64**, 1436 (1960).

32. Freeman, G. R., *J. Chem. Phys.*, **33**, 71 (1960).

33. Dewhurst, H. A., and Schuler, R. H., *J. Am. Chem. Soc.*, **81**, 3210 (1959).

34. Wagner, C. D., *J. Phys. Chem.*, **64**, 231 (1960).

35. Dewhurst, H. A., *J. Phys. Chem.*, **63**, 813 (1959).

36. Ref. 10 p. 18.

37. Ref. 10 p. 126-7.

38. Ref. 9 p. 509.

39. Patrick, W. N., and Burton, M., *J. Am. Chem. Soc.*, **76**, 2626 (1954).

40. Burton, M., Chang, J., Lipsky, S., and Reddy, M. P., *Rad. Res.*, **8**, 203 (1958).

41. Manion, J. P., and Burton, M., *J. Phys. Chem.*, **56**, 560 (1952).

42. Burton, M., Kirby-Smith, J. S., Magee, J. L., "Comparative Effects of Radiation," John Wiley & Sons, Inc., New York, 1960.

43. Melhuish, W. H., *Nature*, **184**, Supplement 25, p. 1933, Dec. 19, 1959.

44. Cundiff, R. H., and Marcunas, P. C., *Anal. Chem.*, **28**, 792, (1956).

45. Bellamy, L. S., "The Infrared Spectra of Complex Molecules," John Wiley & Sons, Inc., New York, 1958.

46. Anon., *Anal. Chem.*, **33**, 480 (1961).

47. Chapiro, A., *J. Phys. Chem.*, **63**, 801 (1959).

48. Schuler, R. H., "Symposium on Radiation Chemistry of Hydrocarbons and Related Substances," Am. Chem. Soc., Sept. 1957, Petroleum Chem. Div.

49. Bretton, R. H., and Swiebel, I., "Investigation of Initial Free Radical Yields in Organic Compounds Subjected to Gamma Radiation," WADD TR 60-127, (1960).

50. Tobolsky, A. V., and Mesrobian, R. B., "Organic Peroxides," Interscience Publishers, Inc., New York, 1954.

51. Ref. 16 p. 40.

52. Burr, J. G., and Strong, J. D., "Some Factors Correlating the Rates of Gas Formation in the Radiolysis of Aromatic Hydrocarbons," *NAA-SR*-4962, July 1960.

53. Burr, J. G., and Scarborough, J. M., J. Phys. Chem., 64, 1367 (1960).

54. Ref. 10 p. 128.

55. Burr, J. G., J. Phys. Chem., 61, 1483 (1957).

56. Beynon, J. H., Lester, G. R., Williams, A. E., J. Phys. Chem., 63, 1861 (1959).

57. Baxter, R. A., and Keen, R. T., Anal. Chem., 31, 475 (1959).

58. Felton, H. R., "I.S.A. Proceeding," International Gas Chromatography Symposium, 1957.

59. Dimbat, M., and Stross, F. H., Anal. Chem., 29, 1517 (1957).

60. Bonnar, R. U., Dimbat, M., and Stross, F. H., "Number Average Molecular Weights," Interscience Publishers, New York 1958, Chap. IV.

61. Burton, M., Ghormley, J. A., and Hochanadel, C. J., Nucleonics, 11, 75 (1955).

62. Weiss, J., Nucleonics, 10, (1952).

63. Sax, K, J., Saari, W. S., Mahoney, C. L., and Gordon, J. M., J. Org. Chem., 25, 1590 (1960).

64. Mahoney, C. L., Kerlin, W. W., Barnum, E. R., Sax, K. J., Saari, W. S., Williams, P. H., "Engine Oil Development," WADC TR 57-177, Pt. II, (1958).

65. Goldschmidt, S., Ber., 55, 636 (1922).

Denver Research Institute, Denver 10, Colo.
Determination of the Relation Between Structure and Radiation Stability of Aryl Ether Fluids, by George E. Bohner, Josef J. Schmidt-Collérus and James H. Weber, July 1961 107 p. tables (Proj. 0(8-7021) WADD TR 60-282-Pt. II) (Contract AF 33 (616)-7220) Unclassified report.

The polyphenyl ethers are of interest as potential lubricants because of their demonstrated resistance to thermal and radiolytic degradation.

1. Radiation-Effect on Compounds

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Gamma radiolytic degradation of the aryl ethers forms polymers which are responsible for the observed viscosity increases. Higher molecular weight aryl ethers are more stable toward radiolysis than diphenyl ether. Diphenyl ether is degraded by polymerization reactions and by the reactions of the phenyl and phenoxy-free radicals resulting from carbon-oxygen bond scission. Radiolytically formed phenol results from the reaction of the phenyl radical at the ortho position of the ether. The phenoxy radical forms diphenoxybenzenes.